J-57

ENTRANCE EXAMINATION-2015

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 - 14** (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 questions of Part-A carries **ONE** mark only, whereas each question of Part-B carries **FOUR** marks.
5. **There is negative marking. Each wrong answer in Part-A carries -0.33 mark and in Part-B carries -1.32 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.

Useful constants:

Rydberg constant = 109737 cm^{-1}; Faraday constant = 96500 C; Planck constant = 6.625 x 10^{-34} J s; Speed of light = 2.998 x 10^{8} m s^{-1}; Boltzmann constant = 1.380 x 10^{-23} J K^{-1}; Gas constant = 8.314 J K^{-1} mol^{-1}; Mass of electron = 9.109 x 10^{-31} kg; Mass of proton = 1.672 x 10^{-27} kg; Charge of electron = 1.6 x 10^{-19} C; 1 D = 3.336 x 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. Which of the following compounds **does not have** a planar molecular configuration?

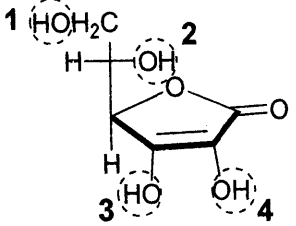
(A) $H_2C=CH_2$

(B) $H_2C=\underset{H}{C}-C\equiv CH$

(C) $H_2C=C=CH_2$

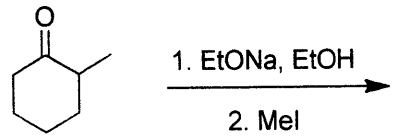
(D) $H_2C=C=C=CH_2$

2. The structural formula for vitamin C is shown below. Of the four hydroxyl groups, identified by circles, which is most acidic?



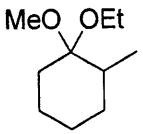
(A) **1** (B) **2** (C) **3** (D) **4**

3. The major product in the following transformation

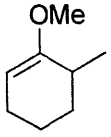


is

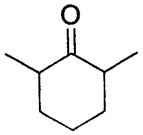
(A)



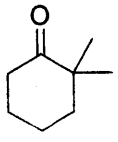
(B)



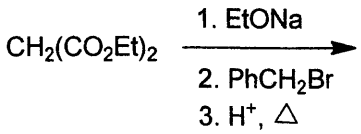
(C)



(D)



4. The product in the following transformation



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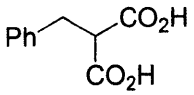
(A)



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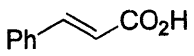

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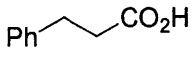
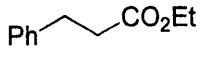


(D)



5. Identify the naturally occurring amino acids, which are having two chiral centres:

(A) Lysine and Arginine
(B) Serine and Phenylalanine
(C) Leucine and Proline
(D) Threonine and Isoleucine

6. The alloy Cu_3Au crystallizes in a cubic lattice with Cu at the face centers and Au at the corners. The number of formula unit/s of the alloy in each unit cell is

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

7. Among octahedral Ti^{2+}, V^{2+}, Ni^{2+} and Cu^{2+} all are expected to show spin-only moments except for the following one which is expected to show both spin and orbital magnetic moments

(A) Ti^{2+} (B) V^{2+} (C) Ni^{2+} (D) Cu^{2+}

8. In tetragonally elongated high-spin $[MnF_6]^{3-}$ the highest energy valence electron of the metal centre resides in

(A) d_{xz} orbital (B) d_{z2} orbital (C) d_{x2-y2} orbital (D) d_{yz} orbital

9. The carbonyl complex following 18-electron rule is

(A) $Cr(CO)_4$ (B) $Mn(CO)_5$ (C) $V(CO)_6$ (D) $Ti(CO)_7$

10. The number of M-M bonds present in $Co_4(CO)_{12}$ is

(A) 3 (B) 4 (C) 5 (D) 6

11. The number of degrees of freedom of water at its triple point is

(A) 0 (B) 1 (C) 2 (D) 3

12. If equal volumes of solutions with pH=2 and pH=7 are mixed, the pH of the resulting solution is:

(A) 9.0 (B) 5.0 (C) 4.5 (D) 2.3

13. The canonical ensemble is represented by a system with

(A) constant ***NVE***. (B) constant ***NVT***.
(C) constant ***μVT***. (D constant ***NPT***.

14. Among the following the well-behaved function is

(A) $e^{-x}[0 \leq x \leq \infty]$ (B) $e^{-x}[-\infty \leq x \leq \infty]$
(C) $e^{-|x|}[-\infty \leq x \leq \infty]$ (D) $\sin^{-1} x\,[-1 \leq x \leq 1]$

15. *trans*-Dichloroethene belongs to the symmetry point group

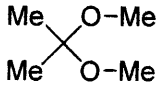
(A) C_{2v} (B) C_{3v} (C) C_{2h} (D) D_{2d}

End of Part-A

Part B

16. A compound with the $C_5H_{12}O_2$ formula has strong infrared absorption in the region 3300 to 3400 cm^{-1}. The ^1H NMR spectrum has three singlets at δ 0.9, δ 3.45 and δ 3.2 ppm with the relative intensities 3:2:1, respectively. The ^{13}C NMR spectrum shows three signals all at less than δ100. Suggest a structure for this compound.

(A)



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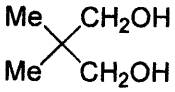

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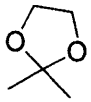
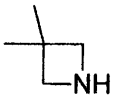
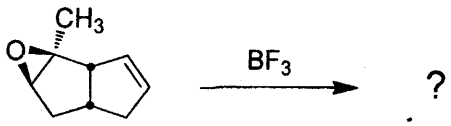


(D)

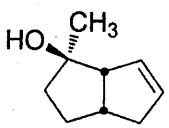


17. The product of the following rearrangement reaction



is

(A)



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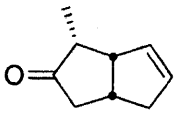

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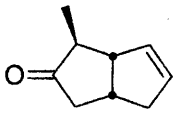

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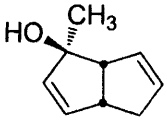
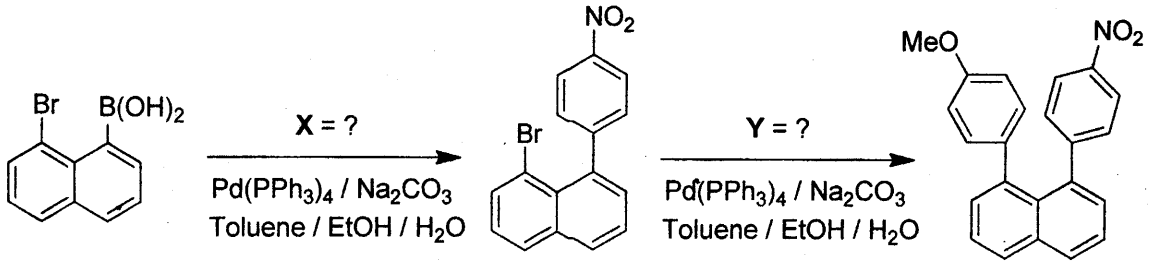


18. The missing reagents in the following transformation



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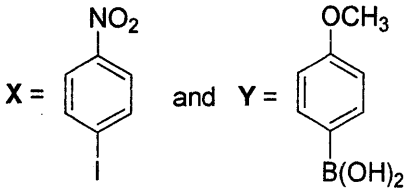
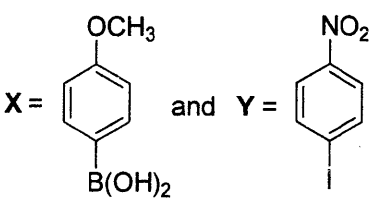
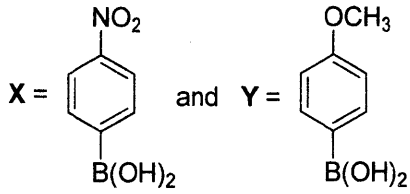
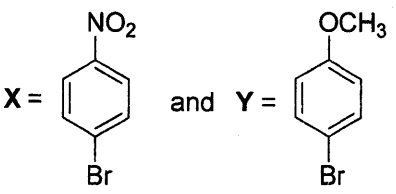
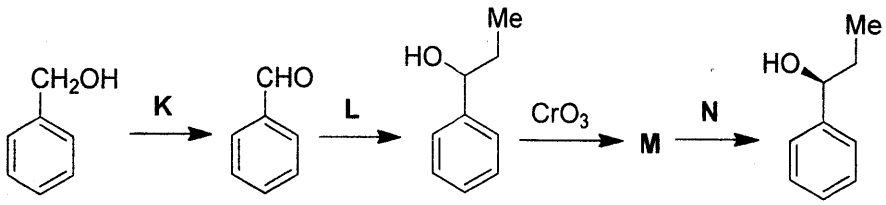
(A) 

(B) 

(C) 

(D) 

19. Identify **K**, **L**, **M** and **N** from the following reaction sequence.



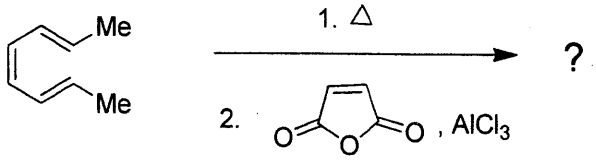
(A) **K** = PCC; **L** = EtMgBr; **M** = PhCOMe; **N** = (*R*)-BINAL-H

(B) **K** = PCC; **L** = EtMgBr; **M** = PhCOEt; **N** = (*S*)-BINAL-H

(C) **K** = CrO_3; **L** = EtMgBr; **M** = PhCOEt; **N** = (*S*)-BINAL-H

(D) **K** = PCC; **L** = EtMgBr; **M** = PhCOEt; **N** = $LiAlH_4$

20. The product obtained in the following transformation



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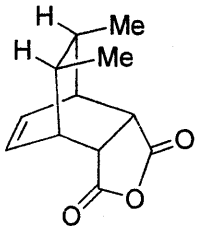
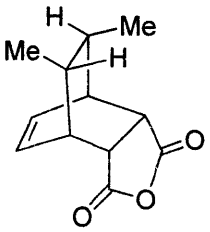
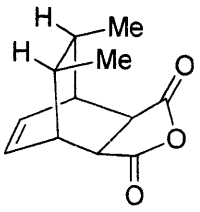
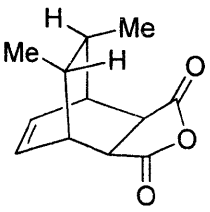
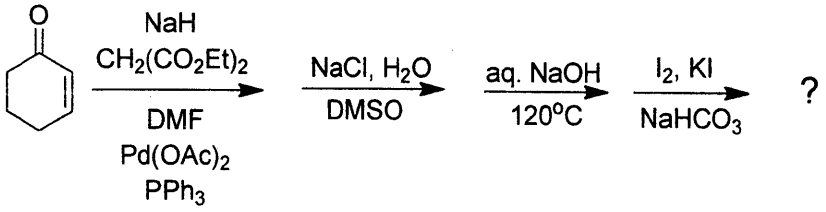
(A) 

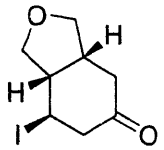
(B) 

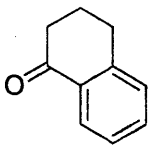
(C) 

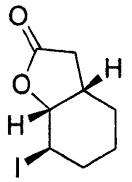
(D) 

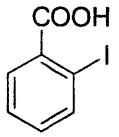
21. The final product of the following sequence of reactions is



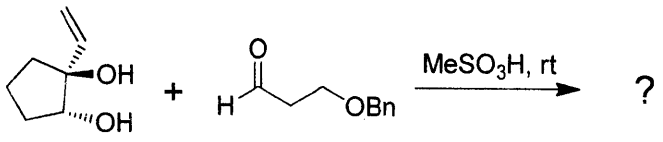
(A) 

(B) 

(C) 

(D) 

22. The product of the following reaction



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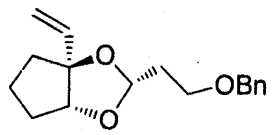
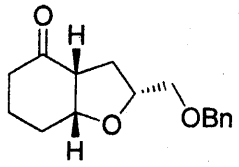
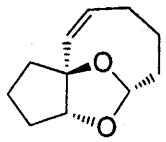
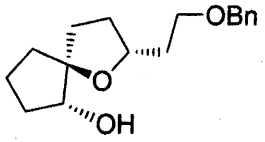
(A) 

(B) 

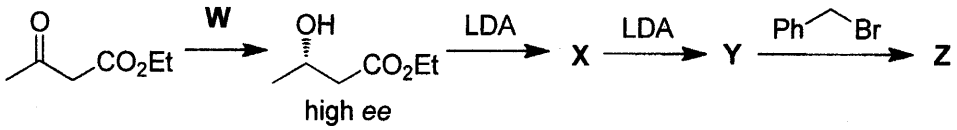
(C) 

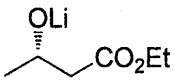
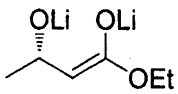
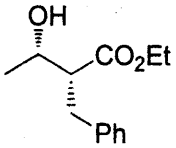
(D) 

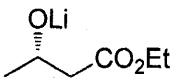
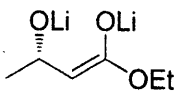
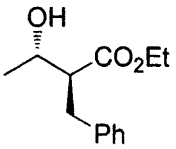
23. If the volume of a typical bacterial cell is 1.0 μm^3, the number of hydrogen ions present in the bacterial cell at pH 7.0 is, approximately:

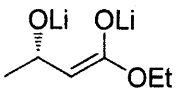
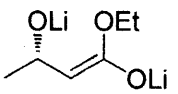
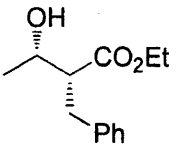
(A) 60 (B) 6×10^2 (C) 6×10^3 (D) 6×10^4

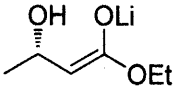
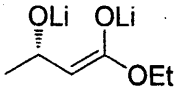
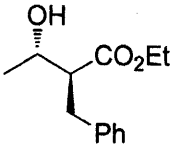
24. Identify **W**, **X**, **Y** and **Z** from the following reaction sequence.



(A) **W:** Baker's yeast **X:**  **Y:**  **Z:** 

(B) **W:** Baker's yeast **X:**  **Y:**  **Z:** 

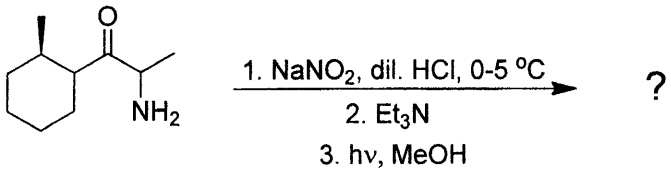
(C) **W:** $BH_3 SMe_2$ **X:**  **Y:**  **Z:** 

(D) **W:** $LiBH_4$ **X:**  **Y:**  **Z:** 

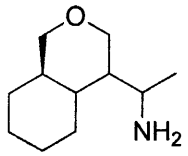
25. The most significant peaks in the mass spectrum of 3-hexanone will be seen at m/z values of:

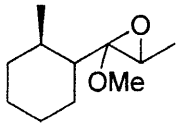
(A) 100, 85, 71, 57
(B) 100, 72, 71, 57
(C) 100, 85, 71, 43
(D) 100, 71, 57, 43

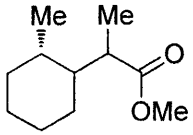
26. The product obtained in the following transformation

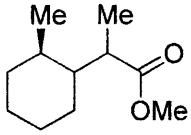


is

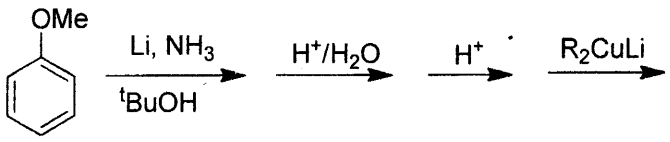
(A) 

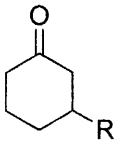
(B) 

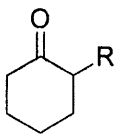
(C) 

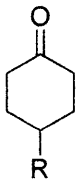
(D) 

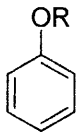
27. The final product of the following sequence of reactions is



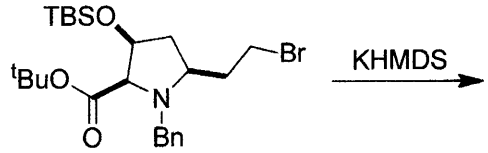
(A) 

(B) 

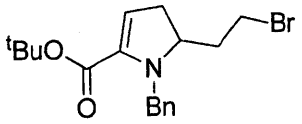
(C) 

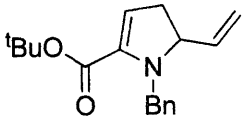
(D) 

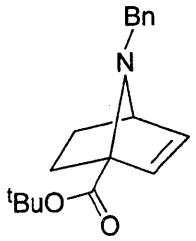
28. The product expected in the following reaction

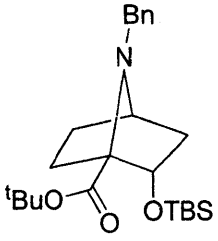


is

(A) 

(B) 

(C) 

(D) 

29. A Trigonal-bipyramidal complex of formula $[M(L\text{-}L)A_2X]$ (A and X are unidentate ligands; L-L represents a bidentate ligand) can have

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

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

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

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

30. The number of isomers for the trigonal bipyramidal molecule PF_3Cl_2 with a non zero dipole moment is

(A) 2 (B) 1 (C) 0 (D) 3

31. The equilibrium constant (K) for the reaction $(CH_3)_2NH_2^+ + (CH_3)_3N \rightleftharpoons (CH_3)_2NH + (CH_3)_3NH^+$ is 960 at 25°C. If the proton affinity of dimethylamine is 930 kJ/mol, what is the proton affinity of trimethylamine? (R = 8.31 J/K mol and the entropy for proton transfer is approximately zero).

(A) 930 kJ/mol (B) 947 kJ/mol (C) 960 kJ/mol (D) 977 kJ/mol

32. The standard reduction potential E° for $Cd^{2+} + 2e^- \rightleftharpoons Cd$ is -0.40 V. What is the value of pH (at $[Cd^{2+}] = 1$ M and pressure of H_2 is 1 bar) above which reduction of Cd^{2+} by H_2 to Cd metal will be spontaneous.

(A) 0 (B) 2 (C) 4 (D) 6

33. The Russel-Saunders ground state term symbols for d^7 and d^9 ions are

(A) $^3F_4$ and $^1S_0$ respectively (B) $^1S_0$ and $^3F_4$ respectively

(C) $^4F_{9/2}$ and $^2D_{3/2}$ respectively (D) $^4F_{9/2}$ and $^2D_{5/2}$ respectively

34. The hardness of a pond water is 6 ppm. The amount of $CaCO_3$ dissolved in 200 mL of that pond water is [1 ppm = 1g of $CaCO_3$ in 10^6mL, atomic mass of Ca = 40]

(A) 1.2×10^{-4} g (B) 1.2×10^{-3} g (C) 2.1×10^{-3} g (D) 3.0×10^{-4} g

35. Using Wade's rule predict the structure of $Os_5(CO)_{16}$

(A) square pyramid (B) trigonal bipyramid

(C) capped tetrahedron (D) butterfly shaped

36. The axial ligands of myoglobin, cytochrome P-450 and catalase respectively are

(A) Imidazole, Thiolate and Phenolate (B) Imidazole, Phenolate and Thiolate

(C) Phenolate, Thiolate and Imidazole (D) Thiolate, Imidazole and Phenolate

37. A sample of pure sodium oxalate ($Na_2C_2O_4$) weighing 0.2856 g is dissolved in water. Excess sulphuric acid is added and the resultant solution is titrated at 70°C, using 45.12 ml of a KMnO4 solution. The end point is overrun and the back titration is carried out with 1.74 ml of 0.0516 M oxalic acid solution. The molarity of the $KMnO_4$ solution is

(A) 0.01969 mmol/ml (B) 0.01969 mol/ml

(C) 0.089784 mmol/ml (D) 2.32819 mmol/ml

38. Reaction of benzene with an alkali metal ion leads to the formation of a radical anion $[C_6H_6]^-$. The electron paramagnetic resonance spectrum of the radical anion involving hyperfine coupling with all six hydrogens will show a [I = ½ for Hydrogen atom]

(A) Seven line pattern (B) One line pattern

(C) Four line pattern (D) Six line pattern

39. Gaseous N_2O_5 when compressed display ionic character in the crystal lattice ($NO_2^+NO_3^-$). Which spectroscopic method can be employed to confirm this transformation?

(A) Nuclear magnetic resonance spectroscopy

(B) Electron paramagnetic resonance spectroscopy

(C) Vibrational spectroscopy

(D) Photoelectron spectroscopy

40. A cell is set up as follows:

$$Fe \mid Fe^{2+} (a = 0.1) \parallel Cd^{2+} (a = 0.001) \mid Cd$$

The voltage of the cell and the equilibrium constant of the cell reactions are,
[$E^o_{Cd^{2+}/Cd} = -0.44$ V, $E^o_{Fe^{2+}/Fe} = -0.40$ V, T = 298 K]

(A) –0.02 V and 23 (B) +0.02 V and 23 (C) +0.04 V and 4.8 (D) –0.02 V and 4.8

41. In the compounds $Co_2(CO)_x$ and $H_yCr(CO)_5$, the numbers x and y are respectively

(A) 8 and 2 (B) 6 and 2 (C) 8 and 1 (D) 6 and 1

42. The molecules CH_3Cl, CCl_4, SO_2 and SiH_4 are

(A) symmetric, spherical, asymmetric and spherical tops
(B) spherical, spherical, symmetric and symmetric tops
(C) asymmetric, symmetric, asymmetric and symmetric tops
(D) spherical, symmetric, asymmetric and symmetric tops

43. ^{199}Hg nucleus has a gyromagnetic ratio of 4.8154×10^{-7} rad T^{-1} s^{-1}. The frequency at which ^{199}Hg will produce an NMR signal at a magnetic field of 1.5 Tesla is

(A) 5.42 MHz (B) 9.81 GHz (C) 10.93 MHz (D) 11.42 MHz

44. In a reversible isothermal expansion at 298 K, an ideal gas changes its volume from V to 2V. What is the change in the molar internal energy of the gas?

(A) +2.27 kJ mol^{-1} (B) 0 J mol^{-1} (C) +1.72 kJ mol^{-1} (D) –2.27 kJ mol^{-1}

45. From fundamental equation $dA = -SdT - PdV$, the Maxwell relation obtained is

(A) $\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial S}\right)_V$ (B) $\left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial P}{\partial T}\right)_V$

(C) $\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_T$ (D) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

46. An element with atomic radius of 1.7 Å forms crystals with a face-centered lattice. In an X-ray diffraction experiment using Cu K_α radiation (λ=1.54 Å), the first order diffraction from the (111) planes will occur at a 2θ value of :

(A) 13.0^0 (B) 16.8^0 (C) 32.2^0 (D) 64.9^0

47. At 25 ^{0}C the values of Λ^∞ are: sodium benzoate, 82.5×10^{-4} S m^2/mol: hydrochloric acid, 426.2×10^{-4} S m^2/mol: sodium chloride, 126.5×10^{-4} S m^2/mol. The Λ^∞ for benzoic acid will be

(A) 217.2 S m^2/mol (B) 299.7 S m^2/mol (C) 382.2 S m^2/mol (D) 343.7 S m^2/mol

48. The value of the vibrational partition function for I_2 ($\tilde{\nu}$ = 208 cm^{-1}) at 300 K is given by (hc/kT=0.0483 cm at 298 K)

(A) 0.633 (B) 1.58 (C) 1.37 (D) 0.73

49. 0.1135 gm of TNT releases 410 calories of heat upon explosion at 27 °C. One mole of TNT produces three moles of CO and two moles of N_2 on explosion. When one mole of TNT explodes at 27 °C, the ΔH is

(A) –817 kcal (B) –612 kcal (C) –534 kcal (D) –1022 kcal

50. Normalization constant of the wave function $\psi = \cos(^{n\pi x}/_{a_0})$ $[0 \le x \le a_0; n = 0,1,2, \ldots.]$ is

(A) a_0 (B) $\sqrt{2/a_0}$ (C) $\sqrt{a_0/2}$ (D) $2/a_0$

51. The spacing between the lines in the microwave spectrum of $^{39}K^{127}I$ is 3634 MHz. The bond length of $^{39}K^{127}I$ is

(A) ~305 pm (B) ~600 pm (C) ~380 pm (D) ~410 pm

52. The value of $\langle x^2 \rangle$ for the ground state of a harmonic oscillator with mass μ and force constant k is

(A) $\hbar/2\sqrt{\mu k}$ (B) $2\hbar/\sqrt{\mu k}$ (C) $\hbar/2\mu k$ (D) $2\hbar/\mu k$

53. The fundamental and first overtone in the IR spectrum of $^{12}C^{16}O$ occur at 2143 and 4269 cm^{-1}, respectively. The values of $\bar{\nu}_e$ and $\bar{\nu}_e\bar{x}_e$ for $^{12}C^{16}O$ are

(A) 3000 and 100 cm^{-1} (B) 2143 and 13 cm^{-1}

(C) 2169 and 13 cm^{-1} (D) 4260 and 130 cm^{-1}

54. A sample of polystyrene is composed of a series of fractions of different sized molecules as shown in the table below

Fraction	Weight Fraction	Molecular Weight
A	0.10	12000
B	0.19	21000
C	0.24	35000
D	0.18	49000

The weight average molecular weight of this polymer sample is

(A) 32300 (B) 117000 (C) 51760 (D) 22410

55. A drug is known to be ineffective after 30% decomposition. The original concentration of drug sample was 500 units/mL. After 20 months, the concentration decreased to 420 units/mL. Assuming that the decomposition follows a first-order kinetics, the expiry time of this drug will be:

(A) 79.4 months (B) 40.9 months

(C) 80.5 months (D) 49.3 months