C 3366 (Pages : 10) Name.....

Reg. No.....

Ph.D. ENTRANCE EXAMINATION, APRIL 2021

CHEMISTRY

Time : Two Hours Maximum : 100 Marks

Date :

Answer **all** *questions.*

Section A

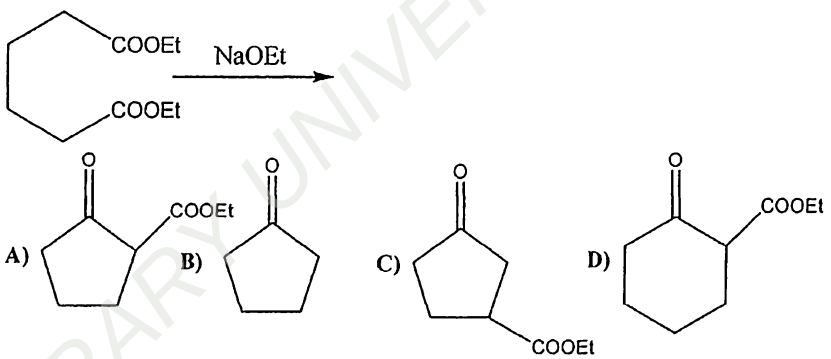
Answer the questions in a **separate** *sheet (provided) ;*
No negative mark for wrong *answers.*

1. The more stable conformation of 2-amino ethanol is :

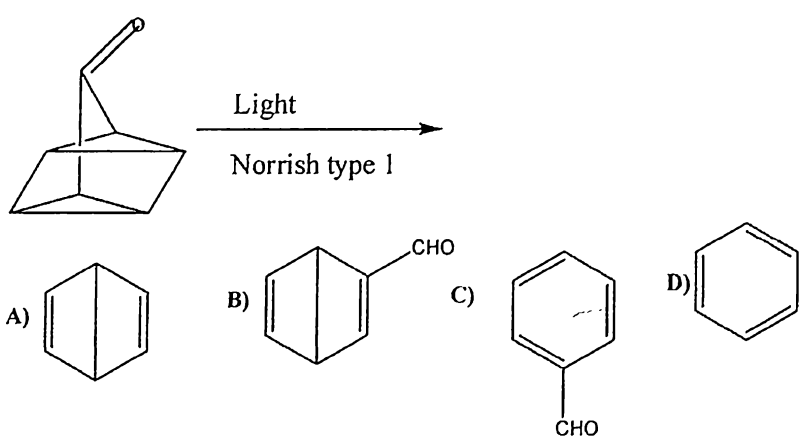
   (A) Anti. (B) Skew.

   (C) Eclipsed. (D) Partially eclipsed.

2. The major product in the following reaction is :



3. The stable final product of the following photochemical reaction is :



4. Ortho - bromo anisole on treatment with KNH_2 in liquid ammonia gives :

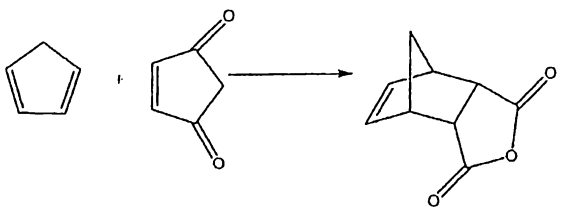
   (A) Meta anisidine.

   (B) Ortho anisidine.

   (C) Para anisidine.

   (D) Mixture of meta and ortho anisidine.

5. The reaction shown below is :



   (A) ${}_{\pi}4_s + {}_{\pi}2_s$ cycloaddition. (B) ${}_{\pi}4_s + {}_{\pi}2_a$ cycloaddition.

   (C) ${}_{\pi}4_a + {}_{\pi}2_s$ cycloaddition. (D) ${}_{\pi}4_a + {}_{\pi}2_a$ cycloaddition.

6. The Reformatsky reaction is often used for the preparing of :

   (A) α - hydroxyl ester. (B) β - hydroxyl ester.

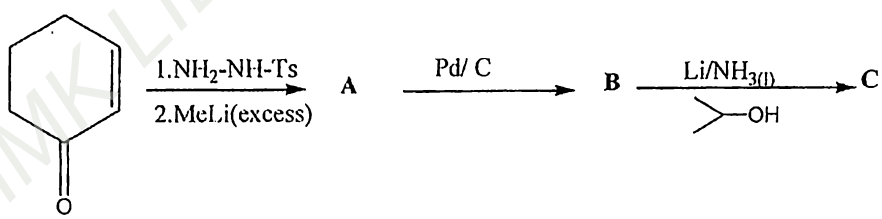
   (C) α - halo ester. (D) β - halo ester.

7. The oxy- Cope rearrangement is a :

   (A) [2, 3] sigmatropic rearrangement. (B) [3, 3] sigmatropic rearrangement.

   (C) [1, 3] sigmatropic rearrangement. (D) [1, 5] sigmatropic rearrangement.

8. The products A, B and C respectively in the reaction are :



   (A) 1, 3-cyclohexadiene, benzene, 1, 4-cyclohexadiene.

   (B) 1, 4-cyclohexadiene, benzene, 1, 3-cyclohexadiene.

   (C) 1, 3-cyclohexadiene, cyclohexane, 1, 4-cyclohexadiene.

   (D) 1, 4-cyclohexadiene, cyclohexane, 1, 3-cyclohexadiene.

9. Acetophenone can be converted to phenol by reaction with :

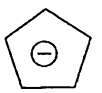
   (A) *m*-CPBA followed by base catalysed hydrolysis.

   (B) Conc. HNO_3.

   (C) Iodine and NaOH.

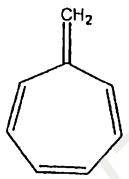
   (D) Singlet oxygen followed by base catalysed hydrolysis.

10. Which of the following molecule is aromatic in nature ?

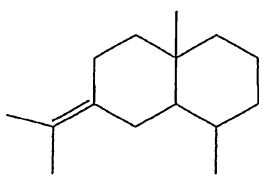
   (A)  .

   (B)  .

   (C)  .

   (D)  .

11. The following compound can be considered as a :



   (A) Monoterpene.

   (B) Sesquiterpene.

   (C) Diterpene.

   (D) Triterpene.

12. Zeta potential is also called :

   (A) Electro-osmosis potential.

   (B) Electro kinetic potential.

   (C) Electro phoretic potential.

   (D) Sedimentation potential.

13. Quantum dots represent which type of nanomaterials ?

   (A) 0-D nanomaterials.

   (B) 1-D nanomaterials.

   (C) 2-D nanomaterials.

   (D) 3-D nanomaterials.

14. Which one of the following is a 'top-down approach' for the synthesis of nanomaterials ?

   (A) CVD.

   (B) Laser Ablation.

   (C) Sol-gel synthesis.

   (D) Co-precipitation.

15. AFM belongs to which type characterization ?

(A) Optical Probe Methods. (B) Electron Probe Methods.

(C) Scanning Probe Methods. (D) Spectroscopic Methods.

16. $C_{59}N$ is a :

(A) Carbon allotrope. (B) Endohedral fullerene.

(C) Heterofullerene. (D) Exohedral fullerene.

17. EDX- Spectrum is a plot of emitted X-ray intensity against its :

(A) Energy. (B) Wavelength.

(C) Frequency. (D) Amplitude.

18. The canonical ensembles are ensembles with constant values for :

(A) E, V and N. (B) E, V and μ.

(C) T, V and N. (D) T, V and μ.

19. For a chemical reaction, the half life of reaction is directly proportional to the initial concentration. The order of the reaction is :

(A) 1^{st} order. (B) Fractional order.

(C) 2^{nd} order. (D) Zero order.

20. $dP/dT = q/T(V_B - V_A)$. This is mathematical form of :

(A) Claussius - Claypeyron equation.

(B) Kirchhoff's equation.

(C) Clausius -Mossotti equation.

(D) Gibbs-Duhem equation.

21. The thermogram in differential thermal analysis (DTA) is obtained by plotting :

(A) dw/dt versus temperature.

(B) ΔT versus temperature.

(C) ΔH versus temperature.

(D) Temperature versus volume.

22. The Debye- Huckel limiting law can be mathematically represented as :

(A) $\log \gamma \pm = -0.509 |z + z -| \ I^{1/2}$.

(B) $\log \gamma \pm = -0.509 |z + z -| \ A^{1/2}$.

(C) $\log \gamma \pm = -0.509 |z + z -| \ c^{1/2}$.

(D) $\log \gamma \pm = -0.509 |z + z -| \ \gamma^{1/2}$.

23. In which polymer of propene, configuration of substituted carbon atom alternates regularly ?

(A) Atactic. (B) Isotactic.

(C) Syndiotactic. (D) None of these.

24. The ground state term symbol for Ce^{3+} ion is :

(A) $^2F_{5/2}$. (B) $^3H_4$.

(C) $^7F_0$. (D) $^6H_{5/2}$.

25. The value of the commutator $[x, d/dx]$ is :

(A) 1. (B) – 1.

(C) 0. (D) 2.

26. The degree of degeneracy for a rigid rotor in an energy level with quantum number J is equal to :

(A) J. (B) 2J.

(C) 2J – 1. (D) 2J + 1.

27. Which of the following is an inverse spinel ?

(A) $MgAl_2O_4$. (B) Mn_3O_4.

(C) $FeCr_2O_4$. (D) $NiFe_2O_4$.

28. According to the HMO treatment, the resonance energy of cyclobutadiene is :

(A) Zero. (B) 4.472 β.

(C) 0.472β. (D) 4α + 4.472 β.

29. The slope of a line in a graph of *k* version 1/T for the reaction is – 5841 K. Then correct mathematical statement is :

(A) Ea/2.303 R = – 5841 K. (B) – Ea/2.303 = – 5841.

(C) Ea = 5841/2.303 R. (D) – Ea/2.303R = – 5841.

30. The total number of fine and hyperfine EPR lines expected for high spin Mn (II) complexes are respectively (I = 5/2 for Mn) :

(A) 3 and 30. (B) 5 and 33.

(C) 5 and 30. (D) 4 and 24.

31. The PMR spectrum of [18]- annulene shows :

(A) Only one peak at δ 7.2 (18H).

(B) Only one peak at δ 5.0 (18H).

(C) Two peak at δ 9.0 (12H) and δ 3.0 (6H).

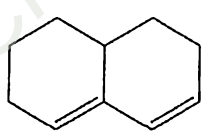
(D) Two peak at δ 9.0 (6H) and δ 3.0 (12H).

32. The ^{19}F NMR spectrum of PF_5 at room temperature (coupled with ^{31}P) consists of :

(A) Triplet. (B) Quintet.

(C) Doublet. (D) Singlet.

33. According to Woodward -Fieser rules, the theoretical value of λ_{max} for the given molecule will be :



(A) 229 nm. (B) 254 nm.

(C) 245 nm. (D) 234 nm.

34. The number of fundamental vibrations of CO_2 is :

(A) Five. (B) Two.

(C) Three. (D) Four.

35. Emission of a second electron after high energy X-rays removes a core electron is known as :

(A) Photovoltaic effect. (B) Zeeman effect.

(C) Debye-Falkenhagen effect. (D) Auger effect.

36. The term Doppler velocity is associated with which spectral method ?

(A) ESR spectroscopy. (B) NQR spectroscopy.

(C) Môssbauer spectroscopy. (D) Auger electron spectroscopy.

37. The point group symmetry of the molecule ferrocene in the staggered form is :

(A) C_3v. (B) D_4h.

(C) D_{5h}. (D) D_{5d}.

38. In DEPT 135 spectrum, which of the following is correct ?

(A) Produce signals for all protonated carbon atoms.

(B) CH and CH_3 peaks are positive and CH_2 peaks are negative.

(C) CH and CH_3 peaks are negative and CH_2 peaks are positive.

(D) Only CH peaks are visible.

39. The sulphur-nitrogen compound that exhibits different colours with temperature is :

(A) $S_4N_4H_4$. (B) S_2N_2.

(C) S_4N_4. (D) $(SN)_X$.

40. In *ino silicates*, number of oxygen shared between silicon atoms will be :

(A) 1. (B) 2.

(C) 3. (D) 4.

41. Which among the following metallocenes is having highest oxidizing power ?

(A) $\left[\left(\eta^5 - Cp\right)_2 Fe\right]$. (B) $\left[\left(\eta^5 - Cp\right)_2 Co\right]$.

(C) $\left[\left(\eta^5 - Cp\right)_2 Mn\right]$. (D) $\left[\left(\eta^5 - Cp\right)_2 Ni\right]$.

42. The *styx* code of B_4H_{10} is :

(A) 4120. (B) 4220.

(C) 4012. (D) 3203.

43. The total electron count (TEC) and structure of the carbonyl cluster $[Os_5C(CO)_{15}]$ is :

(A) 74 and *closo*. (B) 74 and *nido*.

(C) 70 and *closo*. (D) 70 and *arachno*.

44. The W-W bond order in $[W_2(OPh)_6]$ is :

(A) 1. (B) 2.

(C) 3. (D) 4.

45. In solid state the molecule $Co_2(CO)_8$ has :

(A) All terminals CO groups and two Co-Co bonds.

(B) Terminal CO groups , two bridging CO groups one Co-Co bond.

(C) Terminal CO groups , one bridging CO groups one Co-Co bond.

(D) Terminal CO groups, three bridging CO groups two Co-Co bonds.

46. The number of labile sulphur atoms present in 1 Fe-ferredoxin is :

(A) 1. (B) 2.

(C) 3. (D) 0.

47. An element X emits successively two β-particles, one α–particle one positron and one neutron. The mass and atomic number of the element are decreased by :

(A) 4 and 1. (B) 5 and 1.

(C) 3 and 2. (D) 3 and 1.

48. For the reaction $[Fe(CN)_6]^{4-} + [Mo(CN_8)^{3-} \rightarrow [Fe(CN_6)^{3-} + [Mo(CN)_8]^{4-}$ the electron transfer takes place by :

(A) Outer sphere reaction.

(B) Inner sphere reaction.

(C) Induced electron transfer reaction.

(D) Excited state inner sphere mechanism.

49. The oxidation state of the central metal iron in *oxy*-hemoglobin is :

(A) + 4. (B) + 3.

(C) 0. (D) + 2.

50. Which of the following is not a blue protein ?

(A) Azurin. (B) Plastocyanin.

(C) Tyrosine. (D) Umecyanin.

(50 × 1 = 50 marks)

Section B

Each question carries 5 marks.

1. State and explain the selection rules governing electronic transitions.

2. Explain the use of infrared spectroscopy in the study of co-ordination compounds.

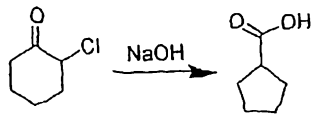
3. Describe the synthesis, structure and bonding of $[Re_2Cl_8]^{2-}$.

4. Discuss the Marcus theory of outer sphere electron transfer reactions.

5. Briefly explain the elimination-addition mechanism in aromatic nucleophilic substitution.

6. Write short note on aromatic, non-aromatic and anti-aromatic molecules based on Huckel theory.

7. Outline a reasonable mechanism for the following transformation :



8. Apply Schrödinger wave equation to a particle in 1D box problem.

9. Briefly explain Joule-Thomson effect. Obtain expression for Joule-Thomson co-efficient.

10. Discuss the stoichiometric point defects shown by crystalline solids.

(10 × 5 = 50 marks)