

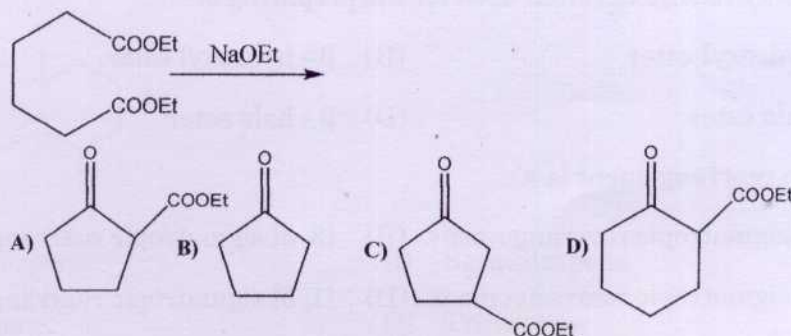
Ph.D. ENTRANCE EXAMINATION, APRIL 2021**CHEMISTRY**

Time : Two Hours

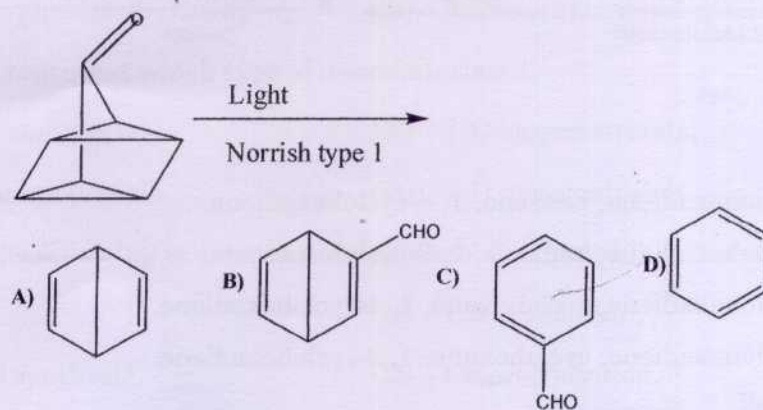
Maximum : 100 Marks

Date : *Answer all questions.***Section A***Answer the questions in a separate sheet (provided) ;***No negative mark for wrong answers.**

- The more stable conformation of 2-amino ethanol is :
(A) Anti. (B) Skew.
(C) Eclipsed. (D) Partially eclipsed.
- The major product in the following reaction is :



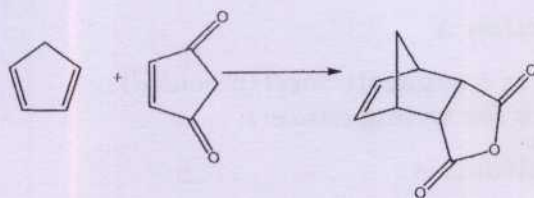
- The stable final product of the following photochemical reaction is :

**Turn over**

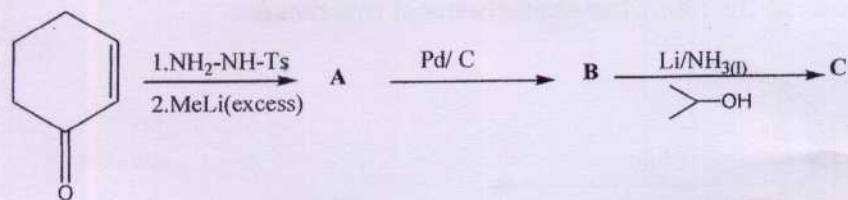
4. Ortho - bromo anisole on treatment with KNH_2 in liquid ammonia gives :

- (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 :

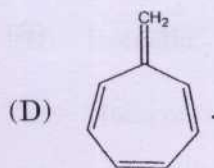
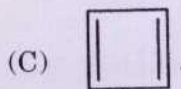


- (A) 1, 3-cyclohexadiene, benzene, 1, 4-cyclohexadiene.
- (B) 1, 4-cyclohexadiene, benzene, 1, 3-cyclohexadiene.
- (C) 1, 3-cyclohexadiene, cyclohexane, 1, 4-cyclohexadiene.
- (D) 1, 4-cyclohexadiene, cyclohexane, 1, 3-cyclohexadiene.

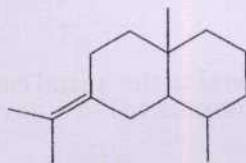
9. Acetophenone can be converted to phenol by reaction with :

- (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 ?



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.

Turn over

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) 1st order. (B) Fractional order.
(C) 2nd 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 :

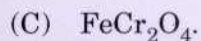
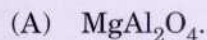
(A) J .

(B) $2J$.

(C) $2J - 1$.

(D) $2J + 1$.

27. Which of the following is an inverse spinel ?



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

(A) Zero.

(B) 4.472β .

(C) 0.472β .

(D) $4\alpha + 4.472 \beta$.

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) $E_a/2.303 R = -5841 \text{ K}$.

(B) $-E_a/2.303 = -5841$.

(C) $E_a = 5841/2.303 R$.

(D) $-E_a/2.303R = -5841$.

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 $\delta 7.2$ (18H).

(B) Only one peak at $\delta 5.0$ (18H).

(C) Two peak at $\delta 9.0$ (12H) and $\delta 3.0$ (6H).

(D) Two peak at $\delta 9.0$ (6H) and $\delta 3.0$ (12H).

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

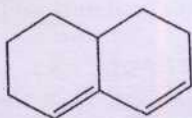
(A) Triplet.

(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) Mössbauer 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) $\text{S}_4\text{N}_4\text{H}_4$. (B) S_2N_2 .
(C) S_4N_4 . (D) $(\text{SN})_x$.

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) $\left[\left(\eta^5 - \text{Cp}\right)_2 \text{Fe}\right]$.

(B) $\left[\left(\eta^5 - \text{Cp}\right)_2 \text{Co}\right]$.

(C) $\left[\left(\eta^5 - \text{Cp}\right)_2 \text{Mn}\right]$.

(D) $\left[\left(\eta^5 - \text{Cp}\right)_2 \text{Ni}\right]$.

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 $[\text{Os}_5\text{C}(\text{CO})_{15}]$ is :

(A) 74 and *closo*.

(B) 74 and *nido*.

(C) 70 and *closo*.

(D) 70 and *arachno*.

44. The W-W bond order in $[\text{W}_2(\text{OPh})_6]$ is :

(A) 1.

(B) 2.

(C) 3.

(D) 4.

45. In solid state the molecule $\text{Co}_2(\text{CO})_8$ has :

(A) All terminal 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 $[\text{Fe}(\text{CN})_6]^{4-} + [\text{Mo}(\text{CN})_8]^{3-} \rightarrow [\text{Fe}(\text{CN})_6]^{3-} + [\text{Mo}(\text{CN})_8]^{4-}$ 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 $\times$ 1 = 50 marks)

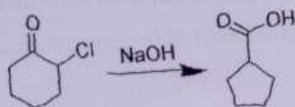
Section B

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 $[\text{Re}_2\text{Cl}_8]^{2-}$.
4. Discuss the Marcus theory of outer sphere electron transfer reactions.
5. Briefly explain the elimination-addition mechanism in aromatic nucleophilic substitution.

Turn over

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)