D 11155 (Pages : 3) Name.....

Reg. No.....

THIRD SEMESTER P.G. DEGREE EXAMINATION, NOVEMBER 2021

(CCSS)

Applied Chemistry

ACH 3C 11—PHYSICAL CHEMISTRY—III

Time : Three Hours Maximum : 80 Marks

Section A

Answer **all** *questions.*
Each question carries 1 *mark.*

Choose the correct answer :

1. According to collusion theory, the pre-experimental factor has ——— dependence on temperature.
   (a) Zero. (b) $T^{1/2}$.
   (c) T. (d) $T^{-1/2}$.
2. The activation energy for a reaction is found to be zero. The reaction rate :
   (a) Increases with temperature.
   (b) Decreases with temperature.
   (c) Independent of temperature.
   (d) Increases with temperature and attains a limiting value.
3. Which of the following is *not* a method of studying fast reactions ?
   (a) Flash photolysis. (b) Pressure jump relaxation spectroscopy.
   (c) Flow methods. (d) Actinometry.
4. Bronsted Bjerrum relationship deals with :
   (a) Primary salt effect.
   (b) Secondary salt effect.
   (c) Effect of dielectric constant of the medium.
   (d) Cage effect.
5. The decay of excited species from higher vibrational level to ground vibrational level of S_1 is called :
   (a) Intersystem crossing. (b) Internal conversion.
   (c) Fluroscence. (d) Phosphorescence.

6. Neodyroium laser si an example of ———— level laser.
   (a) 1. (b) 2.
   (c) 3. (d) 4.
7. Unimolecular gas phase surface catalyzed reactions follow :
   (a) First order kinetics at high pressures and second order kinetics at low pressures.
   (b) First order kinetics at lwo pressures and zero order kinetics at high pressures.
   (c) First order kinetics at low pressures and second order kinetics at high pressures.
   (d) Zero order kinetics at low pressures and first order kinetics at high pressures.
8. Which of the following is not associated with oscillating chemical reactions ?
   (a) BZ. (b) Brusselator.
   (c) Lotka Velterra. (d) Eley-Rideal.
9. Which of the following is not a magic number ?
   (a) 2. (b) 8.
   (c) 18. (d) 50.
10. Which of the following is a moderator in nuclear reactor ?
   (a) Graphite. (b) ^{235}U.
   (c) He. (d) Pb.
11. The trial wave function used in HF method is of determinantal form because :
   (a) It is easier to calculate the integrals.
   (b) For computational simplicity.
   (c) To incorporate indistinguishability.
   (d) To incorporate antisymmetry.
12. 6-31 G* is a :
   (a) Split valence basis set.
   (b) Split valence plus polarization added basis set.
   (c) Split valence plus diffusion added basis set.
   (d) Minimal basis set.

(12 × 1 = 12 marks)

Section B

Answer **all** *questions.*
Each question carries 2 *marks.*

13. Define Steric factor. How is it related to entropy of activation ?
14. What is secondary salt effect ?

15. Explain multiphoton excitation.
16. Distinguish between Vant Hoff complex and Arrhenius complex.
17. Explain Szilard-Chalmer's effect.
18. Distinguish between STO and GTO with examples.

(6 × 2 = 12 marks)

Section C

Answer any **six** *questions.*
Each question carries 6 *marks.*

19. The pre-exponential term for a first order reaction is 5×10^{13} S^{-1} calculate entropy of activation at 300 K.
20. How would you calculate activation energy theoretically ? Explain.
21. When a sample of pure water is heated by a pusle of microwave radiation equilibrium in the water dissociation reaction $H^+ + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O$ is disturbed. The relaxation time for reestablishment of equilibrium at 25° C. is 36 microseconds. Calculate k_1 and k_{-1}. Ion product of water at 25° C. is 10^{-14}.
22. Write Hammett equation. Show that it is a linear free energy relationship.
23. Discuss rotating sector method of studying photochemical reactions.
24. Discuss briefly catalysis by co-ordination compounds.
25. Briefly discuss radiation Chemistry of water.
26. Discuss the mechanisms of interaction of radiation with matter.
27. Discuss the features of Gaussian input file.

(6 × 6 = 36 marks)

Section D

Answer any **two** *questions.*
Each question carries 10 *marks.*

28. Discuss briefly absolute rate theory of reaction.
29. Discuss briefly theory and applications of neutron activation analysis.
30. Derive equations to show the effect of (a) dielectric constant of the medium ; (b) ionic strength of the medium on the rate of ionic reactions.
31. Compare Langmuir-Hinshelwood and Eley Redeal mechanism of bimolecular gas phase surface catalysed reactions. How would you distinguish between the two mechanism under a given set of conditions ?

(2 × 10 = 20 marks)

THIRD SEMESTER P.G. DEGREE EXAMINATION, NOVEMBER 2021

(CCSS)

Applied Chemistry

ACH 3C 10—ORGANIC CHEMISTRY—III

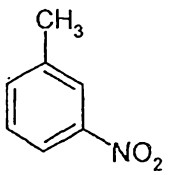
(2019 Admissions)

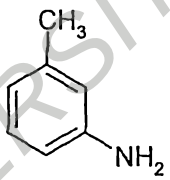
Time : Three Hours Maximum : 80 Marks

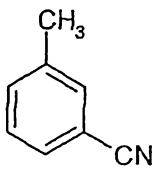
Part A

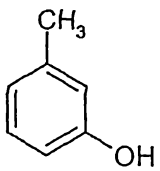
Answer **all** *questions.*
Each question carries 1 *mark.*

1. Which of the following compounds will show the greatest downfield shift for the methyl absorption in ^1H NMR ?

(a) 

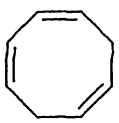
(b) 

(c) 

(d) 

2. Which of the following compounds (assume planar struatcures) would have largest λ_{max} ?

(a) 

(b) 

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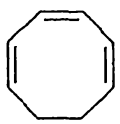
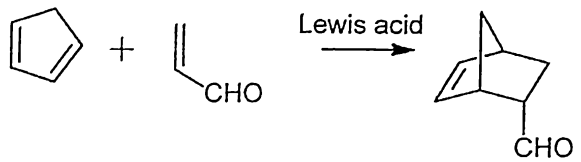
(d) 

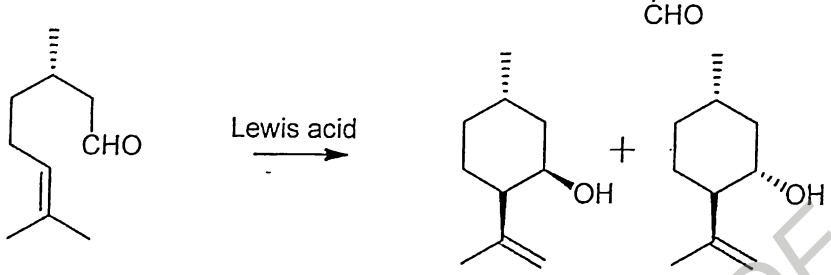
3. Which of the following is NOT an ideal condition for deprotection of acetal protective groups to get the alcohol ?

(a) HCl/Lewis acid. (b) Na/NH_s.

(c) H_2/PdC. (d) $NaOH/H_2O$.

4. Two reactions are given below :



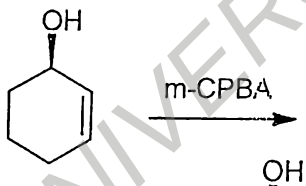


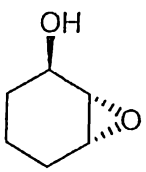
The most appropriate statement with reference to the selectivity of these two reactions is :

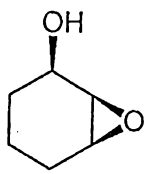
(a) Both stereospecific. (b) Both stereoselective.

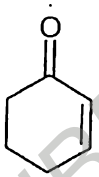
(c) Only one is stereospecific. (d) Only one is steroselective.

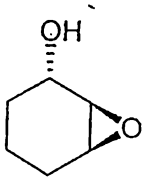
5. The structure of the major product obtained in the following reaction is :



(a) 

(b) 

(c) 

(d) 

6. $NaBH_4$/MeOH can be used effectively for the reduction of :

(a) Only esters. (b) Only ketones.

(c) Only aldehydes. (d) Aldehydes and ketones.

7. Which of the following statement is NOT true for van der Wall forces ?

(a) The energy is approximately 20 kcal/mol.

(b) Exists between almost all atoms and molecules.

(c) Arise from atomic or molecular dipoles.

(d) Statements (b) and (c) are wrong.

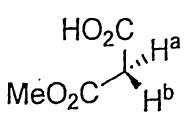
8. Which of the following statement is NOT true about average energies of non-covalent interactions ?
   (a) Electrostatic interactions are stronger than van der Waals interactions.
   (b) Hydrophobic interactions are weaker than hydrogen bonding interactions.
   (c) Covalent bond energies are higher than non-covalent interactions.
   (d) Covalent bond energies are weaker than non-covalent interactions.
9. Which of the following is NOT true about Ugi reaction ?
   (a) It involves an aldehyde, an amine, an isocyanide and a carboxylic acid.
   (b) It involves a ketone, an amine,an isocyanide and a carboxylic acid.
   (c) It involves a ketone, an amine,a nitrile and a carboxylic acid.
   (d) The reaction leads to a bis-amide.
10. Which of the following property is NOT usually associated with flurous solvents?
   (a) Thermal stability. (b) Chemical stability.
   (c) Low toxicity. (d) High polarity.
11. Which of the following is ideal for use in fibres ?
   (a) Melamine-formaldehyde.
   (b) Polyethylene terephthalate.
   (c) Polycarbonate.
   (d) Polyurethanes.
12. The inherent thermal instability of PVC is mainly due to:
   (a) Air oxidation. (b) Thermal decomposition.
   (c) Dehydrochlorination. (d) Hydrolysis.

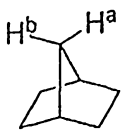
(12 × 1 = 12 marks)

Part B

Answer **all** *questions.*
Each question carries 2 marks.

13. In the following molecules, indicate whether the hydrogens marked H^a and H^b are homotopic, enantiotopic or diastereotopic ? Suggest a spectroscopic technique to distinguish between heterotopic hydrogens :





14. Write down the conditions and reagents used for the protection and deprotection of alcohols as THP ethers. What are its advantages over other alcohol protecting groups ?
15. Indicate two applications of SeO_2 in organic synthesis with examples.
16. Explain the concept of self-assembly with a suitable example.

17. Do you consider Diels-Alder reaction as an atom economic reaction ? Justify.

18. Explain the stereoregularity of polymers using structure of polypropylene as an example.

(6 × 6 = 12 marks)

Part C

Answer any **six** *questions.*
Each question carries six marks.

19. What are the major ionisation techniques used in MS ? Explain the process and discuss the advantages and disadvantages of each with reference to the information expected from the mass spectral data.

20. Identify the spin systems present in *cis*- and *trans*-1, 2-dinitrocyclopropane. Draw line corresponding line spectra. Justify your answer.

21. Discuss the desired characteristics of protecting groups to be used in organic synthesis with appropriate examples in each case.

22. Write a short note on : (a) Synthons and synthetic equivalents ; and (b) Acyl anion equivalents in synthesis.

23. With appropriate examples, illustrate the general concept and applications of phase transfer catalysts.

24. Write a detailed note on structure, properties and applications of calixarenes.

25. Give a short account of solvent free synthesis as a major approach towards green chemistry.

26. Discuss the significance of microwave assisted synthesis and sonochemical synthesis in green chemistry.

27. Write notes on synthesis, structure, properties and applications of:

    (a) Styrene-butadiene rubber. (b) Neoprene.

(6 × 6 = 36 marks)

Part D

Answer any **two** *questions.*
Each question carries 10 *marks.*

28. (a) Based on mass spectral fragmentation pattern, how will you differentiate between methyl butyrate and propyl acetate ? Write down major fragmentation modes.

    (b) What are the criteria for selecting hydroxyl protecting groups in a multistep synthesis ?

29. Discuss the important principles of retrosynthetic analysis with suitable examples.

30. Give a detailed account of various intermolecular forces involved in molecular recognition.

31. (a) Discuss the applications of complex metal hydrides in the reduction of polar multiple bonds in organic compounds.

    (b) Give a short account of the strategies involved in protecting amino groups and carbonyl groups.

(2 × 10 = 20 marks)

D 11153 (Pages : 3) Name.....

Reg. No.....

THIRD SEMESTER P.G. DEGREE EXAMINATION, NOVEMBER 2021

(CCSS)

Applied Chemistry

ACH 3C 09—INORGANIC CHEMISTRY—III

(2019 Admissions)

Time : Three Hours Maximum : 80 Marks

Section A

Answer **all** *questions.*
Each question carries 1 *mark.*

1. Photoisomerization reaction of $[Co(NH_3)_5ONO]^{2+}$ to $[Co(NH_3)_5NO_2]^{2+}$ takes place by an intramolecular process, because ————.

   (a) NO_2^- has a bent structure.

   (b) The reaction takes place in aqueous medium.

   (c) The reaction takes place by ligand substitution process.

   (d) The reaction takes place in presence of a catalyst.

2. The photochemical reaction ; $[Co(CN)_5(H_2O)]^{2-} + I^- \rightarrow [Co(CN)_5I]^{3-} + H_2O$ is an example for ———— reaction.

   (a) Photooxidation reduction. (b) Photoanation.

   (c) Photoaquation. (d) Photosubstitution.

3. When acetate group is bonded to a metal ion in a monodentate fashion, the difference between $v_{asy}COO^-$ and $v_{sym}COO^-$ will be ————.

   (a) between 150-160 $cm.^{-1}$ (b) $> 200\ cm.^{-1}$

   (c) between 100-110 $cm.^{-1}$ (d) cannot be predicted.

4. The ^1H NMR spectrum of PMe_3 is expected to show ————.

   (a) a doublet. (b) a singlet.

   (c) a triplet. (d) a multiplet.

5. The Mössbauer spectra of $K_4[Fe(CN)_6]$ and $K_2[Fe(CN)_5NO]$ consist respectively ———.

   (a) 1 line each. (b) 2 lines each.

   (c) 1 and 2 lines. (d) 2 and 4 lines.

Turn over

6. Which of the following compounds is ESR active ?

(a) $VOSO_4$. (b) $K_2Cr_2O_7$.

(c) $KMnO_4$. (d) $[Co(NH_3)_6]Cl_3$.

7. The correct set of biologically essential elements is ————.

(a) Fe, Co, Cu, Ru. (b) Fe, Mo, Cu, Zn.

(c) Cu, Mn, Zn, Ag. (d) Fe, Ru, Zn, Mg.

8. Excess of ———— causes anaemia by interfering with the biosynthesis of porphyrin required in hemoglobin.

(a) Co. (b) Pb.

(c) Cu. (d) Fe.

9. Myoglobin is a ————.

(a) Timer. (b) Dimer.

(c) Monomer. (d) Tetramer.

10. Deoxyhemoglobin is ————.

(a) Five co-ordinated complex.

(b) High-spin complex.

(c) Fe^{2+} co-ordinated with four N-atoms.

(d) All the above.

11. The metalloenzyme responsible for the removal of hydrogen peroxide is ————.

(a) Ferritin. (b) Catalase.

(c) Dismutase. (d) Hydrogenase.

12. In biological systems, the metal ions involved in electron transport are ————.

(a) Zn^{2+} and Mg^{2+}. (b) Na^+ and K^+.

(c) Ca^{2+} and Mg^{2+}. (d) Cu^{2+} and Fe^{2+}.

(12 × 1 = 12 marks)

Section B

Answer **all** *questions.*
Each question carries 2 *marks.*

13. Give one example for photodissociation reaction in metal complex. Why such reaction can seldom be observed in solution ?

14. What happens to the v(C=N) stretching frequency in N-salicylideneaniline when it gets co-ordinated to Cu^{2+} ion ?

15. Predict the EPR spectrum of $\left[Mn(H_2O)_6\right]^{2+}$.

16. How does proline differ from phenylalanine ? Identify the co-ordination sites in these compounds.
17. What are ionophores ? What is the basis of their classification ?
18. Does dioxygen binding affect the spin state of iron in hemoglobin ? Substantiate your answer.

(6 × 2 = 12 marks)

Section C

Answer any **six** *questions.*
Each question carries 6 *marks.*

19. Distinguish between Prompt and Delayed photochemical reactions.
20. Explain the bonding modes of nitrate group $\left(NO_3^-\right)$ towards a metal ion. How IR spectroscopy can be used to identify these bonding modes ?
21. Explain zero field splitting and Kramer's degeneracy.
22. Bring out the biological importance of nitric oxide.
23. Discuss the role of calcium in biological systems.
24. Explain the role of Mg and Mn in photosynthesis process.
25. Describe the factors that affect the metal-ligand (M-L) vibrations in transition metal complexes.
26. Write a note on biomineralisation.
27. Describe the structure and functions of SOD.

(6 × 6 = 36 marks)

Section D

Answer any **two** *questions.*
Each question carries 10 *marks.*

28. Give an account of the photochemical reactions of Chromium (III), Cobalt (III) and Ruthenium (III) complexes.
29. Discuss the theory involved in Mössbauer spectroscopy. How this technique is useful in the structural investigation of iron complexes ?
30. Compare the structure and functions of hemoglobin, hemerythrin and haemocyanin.
31. What are cytochromes ? How are they classified ? Discuss the structure and functions of cytochrome P_{450}.

(2 × 10 = 20 marks)