D 12253 **(Pages : 4)** **Name.....**

Reg. No.....

FIRST SEMESTER P.G. DEGREE EXAMINATION, NOVEMBER 2021

(CCSS)

Applied Chemistry

ACH 1C 04—PHYSICAL CHEMISTRY—I

(2019 Admissions)

Time : Three Hours Maximum : 80 Marks

Section A

Choose the correct answer.

1. Which of the following Maxwell relations is incorrect ?

   (a) $\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V$.

   (b) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$.

   (c) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$.

   (d) $\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$.

2. Ideal solutions have :

   (a) $\Delta u_{mix} = 0, \Delta H_{mix} = 0$.

   (b) $\Delta H_{mix} = 0, \Delta S_{mix} = 0$.

   (c) $\Delta S_{mix} = 0, \Delta G_{mix} = 0$.

   (d) $\Delta G_{mix} = 0, \Delta H_{mix} = 0$.

3. At steady state :

   (a) Forces and fluxes are zeros.

   (b) Forces and fluxes are non-zeros, but constant.

   (c) Forces and fluxes are non-zeros and decreasing.

   (d) Forces and fluxes are non-zeros and increasing.

4. For irreversible process :

   (a) Direct phenomenological co-efficients one positive and indirect phenomenological co-efficients are negative.

   (b) Direct and indirect phenomenological co-efficients can be positive or negative.

   (c) Both direct and indirect phenomenological co-efficients are always positive.

   (d) Direct phenomenological co-efficients are always positive, indirect phenomenological co-efficients can be positive or negative.

5. According to Debye Hückel theory, thickness of ion atmosphere :

   (a) Increases with ionic strength.

   (b) Decreases with ionic strength.

   (c) Decreases with dielectric constant.

   (d) Independent of ionic strength and dielectric constant.

6. The ionic strength of 0.01 molal $CuSO_4$ solution is :

   (a) 0.01. (b) 0.03.

   (c) 0.04. (d) 0.08.

7. The standard electrode potential of calomel electrodes is 0.2802 V. The potential for calomel electrode with 0.01 molal KCl is :

   (a) 0.2802 V. (b) 0.1620.

   (c) 0.2211. (d) 0.3895.

8. Which of the following statements is true about liquid junction potential :

   (a) It is independent of the ionic mobility.

   (b) It can be eliminated by using a salt bridge.

   (c) It can be minimised by using a salt bridge.

   (d) It can be determined by EMF measurements using a cell without transference.

9. Which of the following is *not* correct for over voltage :

   (a) It depends on electrode kinetics.

   (b) It depends on the resistance of the electrolyte.

   (c) Back e.m.f. contributes towards over voltage.

   (d) It can be eliminated by platinized platinum.

10. Which of the following is *not* correct for polarography ?

    (a) Diffusion current is proportional to concentration of electrolyte.

    (b) Migration current is plotted against applied voltage.

    (c) Ilkovic equation is valid.

    (d) Cathode is dropping mercury electrode.

11. The total number crystal point groups is :

    (a) 6. (b) 7.

    (c) 14. (d) 32.

12. The Schoenflies symbol corresponding to mmm (Hermann Maugan) is :

(a) D_{2h}. (b) D_{2d}.

(c) C_{2h}. (d) C_{2v}.

(12 × 1 = 12 marks)

Section B

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

13. Show that $\left(\frac{\partial u}{\partial v}\right)_T = \frac{a}{v^2}$ for a van der Waals gas (a- van der Waals constant).

14. State and explain Onsager reciprocal relation.

15. Write Debye-Hückel Onsager equation. How is it verified ?

16. Calculate the EMF of the cell $Zn \left| \begin{matrix} Zn^{2+} \\ a = 0.04 \end{matrix} \right| \left| \begin{matrix} Cd^{2+} \\ a = 0.0002 \end{matrix} \right| Cd$. The standard electrode potentials of Zn and Cd are – 0.767 and – 0.403 V respectively.

17. 800 mA of current is passed through an aqueous solution of $CuSO_4$ for 20 minutes. What are the products at a node and cathode. Estimate the products.

18. Show that 5-fold axis of symmetry does not exist.

(6 × 2 = 12 marks)

Section C

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

19. Derive Gibbs Duhem equation. Using the equation show that solvent obeys Raults law in the limit of solute obeying Henry's law.

20. For one component system with heat and matter transport derive an equation for the rate of entropy production.

21. Rationalise thermal osmosis using irreversible thermodynamics.

22. Calculate the mean ionic activity co-efficient of 0.01 molal $CaCl_2$ in water at 25° C. A = 0.509 (Use Debye-Hückel limiting law.)

23. The EMF of the cell $Pt \left| \begin{matrix} H_2 \\ 1b \end{matrix} \right| \begin{matrix} HBr \\ 0.1\ m \end{matrix} \left| \begin{matrix} AgBr \\ (s) \end{matrix} \right| Ag$ at 25° C is 0.3524 V. Calculate the mean ionic activity co-efficient of 0.1 m HBr. The standard electrode potential of $\bar{B}r \left| AgBr_{(s)} \right| Ag$ is 0.2224 V.

24. Briefly discuss one of the theories of hydrogen over voltage.

25. What is Tafel plot ? Explain the significance of slope and intercept of Tafel plot.

26. What do you mean by 'systematic absences' ? How do you account for it ?

27. Explain the term 'structure factor'. Discuss its significance.

(6 × 6 = 36 marks)

Section D

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

28. Rationalise electrokinetic phenomenon using irreversible thermodynamics.

29. (a) According to Debye Hückel theory $-\log f_i = A_{zi}^2 \sqrt{Z}$. Show that $-\log fz = A_{3+3-}\sqrt{I}$.

    (b) How do you test the validity of Debye-Hückel limiting law ?

30. Define over voltage. What are the contributing factors of over voltage ? Discuss.

31. Briefly discuss powder method of X-ray analysis.

(2 × 10 = 20 marks)

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Reg. No.....

FIRST SEMESTER P.G. DEGREE EXAMINATION, NOVEMBER 2021

(CCSS)

Applied Chemistry

ACH 1C 03—ORGANIC CHEMISTRY—I

(2019 Admissions)

Time : Three Hours Maximum : 80 Marks

Section A

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

1. Radical induced chlorination of branched alkanes leads to ————————.

   (a) Substitution at branching producing tertiary alkyl chlorides only.

   (b) Mixtures of alkyl chlorides with more of secondary alkyl chloride than primary alkyl chloride.

   (c) Mixtures of alkyl chlorides with more of primary alkyl halide.

   (d) Primary alkyl chlorides exclusively.

2. 2-Heptane is expected to undergo substitution when treated with N-bromosuccinimide and benzoyl peroxide on ———————— predominantly.

   (a) carbon C^1. (b) carbon C^2.

   (c) carbon C^3. (d) carbon C^4.

3. The conversion of C_6H_5-CO-NH-OH to aniline uses ————————.

   (a) i.Br_2 /ii.Aq base. (b) HN_3.

   (c) i. $MeC_6H_4SO_2Cl$ /ii. Aq base. (d) HNO_2.

4. The conversion of 2-chlorocyclohexanone to cyclopentylcarboxylic acid by treatment with aq. NaOH followed by acidification involves ———————— as an intermediate.

   (a) A carbene. (b) A cyclopropanone.

   (c) A cyclopropenone. (d) A carbocation.

Turn over

5. Atropisomerism is exhibited by some ————————.

(a) Allenes.
(b) Allenes and biphenyls.
(c) Biphenyls.
(d) Biphenyls and binaphthyls.

6. ———————— is optically active.

(a) 6-Nitrobiphenyl-2,2'-dicarboxylic acid.
(b) 2,6-Dinitrobiphenyl-2',6'-dicarboxylic acid.
(c) 6,6'-Dinitrobiphenyl-2,2'-dicarboxylic acid.
(d) Biphenyl-2',6'-dicarboxylic acid.

7. 3-Methylbut-3-en-2-one can be obtained from 2-butanone by ————————.

(a) Eschenmoser reaction.
(b) McMurry coupling.
(c) Nef reaction.
(d) Carbene insertion.

8. Corey-Fuchs reaction is a ———————— step process, that involves ————————.

(a) Two ; a N ylide in the first step.
(b) Two; a P ylide in the first step.
(c) Two ; a P ylide in the second step.
(d) one; a carbene in the first step.

9. Barton reaction can best be described as a———————— reaction.

(a) Radical.
(b) Photochemical, remote functionalization.
(c) Radical, remote functionalization.
(d) Radical, photochemical, remote functionalization.

10. Cyclopropanes can be accessed by ————————.

(a) Photolysing a 1,4-diene.
(b) Photolysing an alkene - ketone mixture.
(c) Photolysing a 1,3-diene.
(d) Photolysing an alkyl chloride.

11. HN=NH————————

(a) Reacts with alkynes and alkenes.

(b) Reacts only with alkenes.

(c) Reacts with ketones and alkenes.

(d) Reacts with ketones, alkynes and alkenes.

12. Swern oxidation of $PhCH_2CH_2OH$ is expected to afford ————————.

(a) PhCHO. (b) $PhCH_2CHO$.

(c) $PhCH_2COOH$. (d) $PhCH_2CHO$ and $PhCH_2COOH$.

(12 × 1 = 12 marks)

Section B

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

13. How can singlet and triplet carbenes can be distinguished by a chemical reaction ?

14. Which product in each case would form when benzyltrimethylammonium bromide is treated respectively with :

(i) sodamide in liq. ammonia ?

(ii) conc. aqueous sodium hydroxide solution ?

15. Which isomer(s) of dimethylallene is(are) optically active and why ?

16. Between Et-CO-Et and *n*-Pr-CO-Me, one produces ethylene, among other products, upon photolysis. Which one and why ?

17. How can caprolactam be obtained by an industrial photochemical reaction ?

18. Suggest the reagents useful in coupling phenol oxidatively. What would the product(s) be ?

(6 × 2 = 12 marks)

Section C

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

19. Discuss the factors that control the stability and life time of carbon free radicals.

20. Explain the formation, structure and reactivity of nitrenes.

Turn over

21. Write the mechanism of (i) hydroperoxide and benzidine rearrangements.

22. Describe how the energy content of *n*-butane changes with dihedral angle as it rotates along the central C-C bond.

23. Discuss the cyclic structure of D-xylose and D-ribose stressing on their ring size and conformations.

24. Explain the mechanism of (i) Barbier coupling reaction ; and (ii) Evans aldol reaction.

25. Write a brief note on (i) photoreactions in the atmosphere ; and (ii) photoreactions of arenes.

26. Describe the oxidative cleavage of (i) alkenes ; and (ii) alkynes.

27. Discuss the mechanism and use of (i) Muffat oxidation ; and (ii) diimide reduction.

(6 × 6 = 36 marks)

Section D

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

28. With examples, describe the rearrangement, fragmentation, intramolecular and addition reactions of carbon free radicals.

29. (a) Discuss the structural features that lead to chirality in biphenyls. How can the configuration of chiral biphenyls be specified by the Cahn-Ingold-Prelog nomenclature ?

    (b) Explain with example asymmetric synthesis.

(6 + 4 = 10 marks)

30. (a) Write a concise account of photoreactions of acyclic and cyclic ketones.

    (b) Describe Patterno-Buchi reaction and photochemical dienone rearrangement.

(6 + 4 = 10 marks)

31. Discuss the catalysts used, stereochemical aspects and selectivity in catalytic hydrogenation reactions of compounds with carbon-carbon unsaturated bonds.

[2 × 10 = 20 marks]

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FIRST SEMESTER P.G. DEGREE EXAMINATION, NOVEMBER 2021

(CCSS)

Applied Chemistry

ACH 1C 02—INORGANIC CHEMISTRY—I

(2019 Admissions)

Time : Three Hours Maximum : 80 Marks

Section A

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

1. The actinides which show +7 oxidation states are ————————.

   a) U and Np. b) Am and Pu.

   c) Am and Cm. d) Np and Pu.

2. Most likely, the lanthanide elements will occur with ————————.

   a) Sulphide minerals. b) Chloride minerals.

   c) Phosphate minerals. d) Free metals.

3. Which among the following metal carbonyls can be easily reduced ?

   a) $V(CO)_6$. b) $Cr(CO)_6$.

   c) $Ni(CO)_4$. d) $Fe(CO)_5$.

4. How many metal-metal bonds are present in $[Os_6(CO)_{15}]^{2-}$?

   a) 3. b) 6.

   c) 9. d) 10.

5. Which one shows thermochromism ?

   a) S_4N_4. b) S_2N_2.

   c) $(SN)_X$. d) None of these.

6. Arachno structure of borane obeys the frame work electron formula ————————.

a) $(2n + 3)$. b) $(2n + 6)$.

c) $(2n + 4)$. d) $(2n + 8)$.

7. Carbon nanotubes belong to which structural family ?

a) Polyethane. b) Polyanilines.

c) Fullerenes. d) Carboranes.

8. Which is the technique used to produce nanotubes in sizeable quantities ?

a) Arc discharge. b) Laser ablation.

c) Chemical vapour deposition. d) All the above technique.

9. The most basic species among the following is ————————.

a) F^-. b) OH^-.

c) CH_3^-. d) NH_2^-.

10. Which of the following is a soft acid ?

a) $GaCl_3$. b) CO_2.

c) BF_3. d) SO_3.

11. The number of unpaired electrons of d^7 metal ion in a strong octahedral and tetrahedral ligand fields are ————————.

a) 0 and 4. b) 3 and 4.

c) 1 and 5. d) 1 and 3.

12. The number of ions per mole of the complex $CoCl_35NH_3$ in aqueous solution will be ————————.

a) 8. b) 3.

c) 4. d) 2.

(12 × 1 = 12 marks)

Section B

Answer **all** *questions.*

Each question carries 2 marks.

13. Which is more basic ; $La(OH)_3$ or $Lu(OH)_3$? Give reasons for your answer.

14. Explain HNCC and LNCC with suitable examples.

15. Account for the water-repellent nature of silicones.

16. Why carbon nanotubes are referred to as 'one dimensional' in scientific articles ?

17. What is Symbiosis ?

18. What is nephelauxetic series ?

(6 × 2 = 12 marks)

Section C

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

19. Comment on the magnetic properties of lanthanide complexes.

20. How IR spectroscopy can be used to identify bridging and non-bridging carbonyl groups in metal carbonyls ?

21. Give an account of the classification of carbides with suitable examples.

22. Write a note on dye sensitized solar cells.

23. Differentiate between chelate effect and macrocyclic effect. Why chelate effect is referred to as an entropy effect ? Explain.

24. Diagrammatically represent the d-orbital splitting in square pyramidal and trigonal bipyramidal metal complexes. Explain the reasons for such types of splitting patterns.

25. Discuss the structure and bonding in $[Re_2Cl_8]^{2-}$.

26. Describe the 'top down' and 'bottom up' approaches for the synthesis of nanoparticles, giving suitable examples.

27. What is Jahn-Teller effect ? Comment on its structural and spectral consequences in metal complexes.

(6 × 6 = 36 marks)

Section D

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

28. Bring out the differences between 4f and 5f orbitals and the consequences of these on the properties of lanthanides and actinides. Compare the electronic spectra of lanthanide complexes with those of 3d metal complexes.

29. a) Discuss the importance of icosahedral frame work of boron atoms in boron chemistry.

    b) How is 1, 2-dicarba-*closo*-dodecaborane (12) prepared ? What happens when it is heated ? Comment on the acidity of the different types of hydrogen atoms present in carboranes.

(5 + 5 = 10 marks)

30. Discuss the factors that affect the stability of metal complexes. Describe the spectrophotometric method of determination of stability constant of a metal complex.

31. Critically evaluate valence bond theory, crystal field theory and ligand field theoiy of metal complexes.

[2 × 10 = 20 marks]

D 12250 (Pages : 4) Name.....

Reg. No.....

FIRST SEMESTER P.G. DEGREE EXAMINATION, NOVEMBER 2021

(CCSS)

Applied Chemistry

ACH 1C 01—QUANTUM CHEMISTRY

(2019 Admissions)

Time : Three Hours Maximum : 80 Marks

Section A

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

1. The energy of a particle in 1D box is proportional to :

   a) n. b) n^2.

   c) n^{-1}. d) n^{-2}.

2. The zero point energy for a particle in an infinite potential well for an electron confined to 1nm atom is :

   a) 3.9×10^{-29}. b) 4.9×10^{-29}.

   c) 5.9×10^{-29}. d) 6.9×10^{-29}.

3. If ψ_1 and ψ_2 are two solutions of Schrödinger wave equation, then which of the following is also a solution :

   a) ψ_1/ψ_2. b) $\psi_1\,\psi_2$.

   c) ψ_2/ψ_1. d) $\psi_1 + \psi_2$.

4. Two operators, 'I' and 'J', are said to commute when :

   a) I = J. b) I + J = 0.

   c) IJ = JI. d) $I^2 = J^2$.

5. Which of the following can be quantum numbers for an orbital :

   a) $n = 4, l = 4, m = 3$. b) $n = 2, l = 3, m = 1$.

   c) $n = 3, l = 2, m = -1$. d) $n = 3, l = 0, m = -3$.

6. Arrange in the increasing number of radial nodes : 3p, 4s, 1s, 5d :

a) 1s <3p < 4s < 5d.
b) 1s < 4s < 3p < 5d.
c) 1s < 3p < 5d < 4s.
d) 5d < 1s < 3p < 4s.

7. Zeeman effect is the splitting of spectral line in the presence of :

a) Magnetic field.
b) Electric field .
c) Vaccuum.
d) Inert environment.

8. The ground state term symbol for Cr^{2+} is :

a) ^3P.
b) ^2D.
c) ^3D.
d) ^5D.

9. Which of the following statement is true for Hartree Fock wave function of an atom :

a) It is the product of one electron wave functions.
b) It is symmetrical.
c) It does not obey Pauli's antisymmetry principle.
d) It is in a determinant form.

10. The orbital degeneracy of the level of a one -electron atomic system with Z = 5 and energy ~ –13.6 eV, is :

a) 25.
b) 1.
c) 5.
d) 36.

11. The new term appearing in Hartree Fock energy expression starting from Lithium onwards :

a) Exchange integral.
b) Electronic kinetic energy terms.
c) Electron nuclear attraction terms.
d) Coulomb integral.

12. Perturbation Hamiltonian term of Helium atom corresponds to :

a) Inter electronic repulsion.
b) Electronic kinetic energy.
c) Nucleus-electron attraction.
d) Nuclear kinetic energy.

(12 × 1 = 12 marks)

Section B

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

13. Construct kinetic energy operator from its classical expression.

14. What is the form of Hermite equation and its solution ?

15. Define Hermitian operator.

16. Calculate J = 0 to J = 1 rotational transition energy of the O_2 molecule with a bond length of 121 pm.

17. What are spin orbitals ?

18. Write down the Slater determinant for Be atom.

(6 × 2 =12 marks)

Section C

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

19. Show that $L_z = -i\hbar \frac{\partial}{\partial \phi}$. Given $L_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$.

20. Discuss i) Eigen value postulate ; and ii) Expectation value postulate.

21. What is the expectation value of the momentum, P_x and P_x^2 for a particle in 1-dimensional box ? Rationalize the results.

22. Demonstrate Pauli's antisymmetry principle for fundamental particles. Also show that Pauli's exclusion principle is a direct consequence of antisymmetry principle.

23. Explain Self-Consistent Field method.

24. Suppose a macroscopic SHO is constructed with a mass of 1×10^{-3} kg and a force constant of 10 Nm^{-1}. Determine the approximate vibrational quantum number for this oscillator when its energy equals the thermal energy at room temperature.

25. What are radial probability distribution functions ? Sketch RDF plots of R_{20}, R_{21}, and R_{52}.

26. Write down the complete wave function form of hydrogen atom. What is the average value of the distance of an electron from the nucleus in 1s state of the hydrogen atom ?

27. Explain the fine structure of lines in Balmer series of hydrogen atom using vector model.

(6 × 6 = 36 marks)

Section D

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

28. Derive first order perturbation equation for wave function and energy.

29. Apply Schrödinger equation for 1D simple harmonic oscillator. Solve for eigen functions and eigen values.

30. State and prove variational theorem. Find the ground state energy of particle in one dimensional box using the trial wave function, $\varphi = x(a - x)$.

31. Write down the Schrödinger equation for Hydrogen atom in spherical polar co-ordinates, separate the variables and solve the Phi equation.

(2 × 10 = 20 marks)