FIRST SEMESTER P.G. DEGREE EXAMINATION, NOVEMBER 2020

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

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

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

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

2. Which of the following is *not* a definition of chemical potential of component i $(i \neq j)$:

(a) $\left(\frac{\partial u}{\partial n_i}\right)_{s, v, n_j}$.

(b) $\left(\frac{\partial H}{\partial n_i}\right)_{s, p, n_j}$.

(c) $\left(\frac{\partial A}{\partial n_i}\right)_{v, T, n_j}$

(d) $\left(\frac{\partial G}{\partial n_i}\right)_{p, v, n_j}$.

3. Which of the following is not true for onsager reciprocal relation :

(a) L-matrix is symmetric.

(b) $L_{12} = L_{21}$.

(c) $L_{11} = L_{22}$.

(d) The indirect effect of a force X_1 on another flux J_2 is the same on the indirect effect of the force X_2 on flux J_1.

4. Flow of current due to temperature difference is called ——— effect.

(a) Soret. (b) Seebeck.

(c) Peltier. (d) Electrokinetic.

5. Debye-Hückel onsager relation is associated with :

(a) Variation of conductance with concentration of electrolyte.

(b) Variation of conductance with square root of concentration of electrolyte.

(c) Variation of activity co-efficient with concentration of electrolyte.

(d) Variation of activity with concentration of electrolyte.

6. The ionic strength of 0.01 $LaCl_3$ is :

(a) 0.01. (b) 0.03.

(c) 0.04. (d) 0.06.

7. The solubility of a sparingly soluble salt can be determined by :

(a) Conductometry. (b) Potentiometry.

(c) Both (a) and (b). (d) None of these.

8. The number of electrons transferred in methanol fuel cell is :

(a) 1. (b) 2.

(c) 4. (d) 6.

9. Overvoltage depends on :

(a) Rate of electron transfer. (b) Electrode material.

(c) Both (a) and (b). (d) None of these.

10. A microelectrode is used in polarography to :

(a) Minimize concentration polarization.

(b) Maximise concentration polarization.

(c) Minimize iR drop.

(d) Minimise activation over potential.

11. A plane cuts the x, y and z axes at $2a$, $3b$ and $1c$ respectively. The Miller indices of the plane is :

(a) 2 3 1. (b) 1 2 3 .

(c) 3 2 6. (d) 3 2 1.

12. In XRD pattern of a cubic crystal interplanar spacing corresponding to ——— distance is missing.

(a) $\frac{a}{\sqrt{3}}$. (b) $\frac{a}{\sqrt{5}}$.

(c) $\frac{a}{\sqrt{6}}$. (d) $\frac{a}{\sqrt{7}}$.

(12 × 1 = 12 marks)

Section B

Answer **all** *questions.*

Each question carries 2 *marks.*

13. One mole of toluene is mixed with 0.5 mole of benzene at 300 K. Calculate enthalpy and entropy of mixing assuming ideal behaviour.

14. Derive an equation for the rate of entropy production for one component system with heat transport only.

15. Write Debye-Hückel limiting law. How is it verified ? Explain.

16. Write cell reactions for a fuel cell under : (a) Acidic medium ; and (b) Alkaline medium.

17. Explain the term 'concentration polarization.

18. Draw stereographic projection for (222) plane.

(6 × 2 = 12 marks)

Section C

Answer any **six** *questions.*

Each question carries 6 *marks.*

19. Define partial molal volume. How is it determined ? Discuss.

20. Define phenomenological co-efficients. Show that direct co-efficients always dominate indirect co-efficients.

21. Rationalise electro-osmosis using irreversible thermodynamics.

22. Calculate the thickness of ion atmosphere around K^+ in 0.01 KCl at 25°C in water Dielectric constant of water is 78.5.

23. Calculate the voltage of the cell at 25°C

$$Zn \left| \underset{a = 0.0004}{Zn^{2+}} \right\| \underset{a = 0.2}{Cd^{2+}} \left| Cd. \right.$$

Write the electrode reaction. Find the equilibrium constant of the reaction. The standard electrode potentials of $Zn^{2+}|Zn$ and Cd^{2+}/Cd are – 0.763 and – 0.403 V respectively.

24. Discuss principle and applications of polarography.

25. Define Overvoltage. What are the contributing factors towards overvoltage ? Discuss.

26. Briefly discuss powder XRD.

27. What do you mean by electron density maps ? Discuss.

(6 × 6 = 36 marks)

Section D

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

28. Derive Debye-Hückel Onsager equation. Discuss.

29. Briefly discuss theories of hydrogen overvoltage.

30. Briefly discuss Fourier Synthesis.

31. Discuss briefly :

    (a) Excess thermodynamic functions.

    (b) Thermal diffusion.

    (c) Determination of liquid junction potential.

(2 × 10 = 20 marks)

D 93543 (Pages : 4) Name.....

Reg. No.....

FIRST SEMESTER P.G. DEGREE EXAMINATION, NOVEMBER 2020

(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. Phenylnitrene can be obtained by the photolysis of ———.

   (a) $C_6H_5NH_2$. (b) $C_6H_5N_3$.

   (c) C_6H_5-N=N-C_6H_5. (d) $C_6H_5N_2Cl$.

2. *Trans*-1,1 -dichloro-2,3-diphenylcyclopropane arises from ——— by reaction with ———.

   (a) Z-PhCH=CHPh ; $CHCl_3$/NaOH.

   (b) Z-PhCH=CHPh ; Cl_2.

   (c) E-PhCH=CHPh ; $CHCl_3$/Aq. NaOH.

   (d) E-PhCH=CHPh ; Cl radical.

3. The conversion of benzyltrimethylammonium halide to N,N-dimethyl-N-(2-methylbenzyl)amine by ——— is a ———.

   (a) conc. aq. NaOH ; Sommelet-Hauser rearrangement.

   (b) NaOH-EtOH ; Stevens rearrangement.

   (c) $NaNH_2$/liq.NH_3 ; Stevens rearrangement.

   (d) $NaNH_2$/liq.NH_3 ; Sommelet-Hauser rearrangement.

4. Among Ph-CO-CO-Ph (A), Me-CO-CO-Me (B), cyclohexa-1,2-dione (C) and Ph-CO-CH_2-CO-Ph (D), ——— can undergo benzilic acid rearrangement.

   (a) Only A. (b) A and B.

   (c) A, B and C. (d) A, B, C and D.

Turn over

5. Consider the most stable conformer of *meso*-2, 3-dichlorobutane. The two chlorine atoms in it will be oriented ———.

   (a) Syn. (b) Anti.

   (c) Gauche. (d) Partially eclipsed.

6. Conformationally biased *t*-butylcyclohexane has ——— in one chair form.

   (a) Unfavourable 1, 3-diaxial interactions.

   (b) Unfavourable 1, 4-diaxial interactions.

   (c) Unfavourable 1, 2-diaxial interactions.

   (d) All the three above unfavourable interactions.

7. One of the reactants in a Barbier coupling leading to C_6H_5-CH(OH)-CH_2-CH=CH_2 can be ———.

   (a) Benzyl bromide. (b) Vinyl bromide.

   (c) C_6H_5-CH(OH)-CH_2-Br. (d) Allyl bromide.

8. C_6H_5-C ≡ C-CH_3 can best be obtained ——— using ———.

   (a) By Castro-Stephens coupling ; CH_3I and C_6H_5-C ≡ C-Cu.

   (b) By Castro-Stephens coupling ; C_6H_5-I and CH_3-C ≡ C-Cu.

   (c) By dehydrohalogenation ; C_6H_5-CH_2CBr_2-CH_3.

   (d) From baezaldehyde and acetaldehyde ; $TiCl_4$/Zn.

9. Photolysis of a mixture of MeCH=CMe_2 and Me_2CO gives ———.

   (a) 2, 2, 3 , 3, 4-pentamethyloxetane only.

   (b) 2, 2, 3, 4, 4-pentamethyloxetane only.

   (c) 2, 2, 3, 3, 4-pentamethyloxetane and 2, 2, 3, 4, 4-pentamethyloxetane.

   (d) 1, 1, 2, 2, 3-pentamethylcyclopropane.

10. The manufacture of ——— from ——— is an example of industrial photochemistry.

    (a) Benzyl chloride ; toluene. (b) *p*-chlorotolune ; toluene.

    (c) *o*-and *p*-chlorotoluene ; toluene. (d) Chlorobenzene ; benzene.

11. Styrene can be obtained from———— by reduction in presence of ————.

(a) Phenylacetylene ; Ru catalyst.
(b) Phenylacetylene ; Pd-$BaSO_4$/Quinoline.
(c) Stilbene ; Pd-$BaSO_4$/Quinoline.
(d) Phenylacetylene ; Pd-$BaSO_4$/Pyridine.

12. 1, 1'-Bi-2-naphthol can be obtained from ———— by ————.

(a) 2-naphthol; oxidative coupling.
(b) 1-naphthol; oxidative coupling.
(c) 1,1' -binaphthalene ; hydroxylation.
(d) 1,1' -binaphthalene ; reaction with singlet oxygen.

(12 × 1 = 12 marks)

Section B

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

13. Identify the product arising from the reaction of *trans*-2-butene with (i) Singlet carbene ; and (ii) triplet carbene respectively.

14. Write the starting materials and reagents used in (i) Dakin ; and (ii) Baeyer-Villiger reactions ?

15. Between α-and β-D-glucopyranose, the latter is more stable whereas between α-and β-D-mannopyranose, the former is more stable. Explain your answer in a conformational point of view.

16. Cyclopent-2-en-1-one can be obtained by Pauson-Khand reaction. What are the reactants and catalyst needed ?

17. 3, 4-Dimethylphenol can be obtained by the photochemical rearrangement of a non-aromatic starting material. Which is the starting material and what is the mechanism ?

18. Illustrate with an example the oxidative cleavage of alkynes.

(6 × 2 = 12 marks)

Section C

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

19. Write a brief account of the formation, structure and reactivity of benzyne.

20. Describe the mechanism and application of (i) Skattebol rearrangement ; and (ii) Wolff rearrangement.

Turn over

21. Discuss the mechanism of any two named reactions in which an isocyanate is an intermediate.

22. Explain with an example each the use of (i) Favorskii rearrangement in ring contraction ; and (ii) Tiffeneau-Demjanov rearrangement in ring expansion. Write the mechanism.

23. Discuss the optival activity of allenes and explain with examples how their configuration can be specified by the CIP system.

24. Explain, with mechanisms :

    (i) Cyclization of divinylketones to cyclopentenones using Lewis acid catalysts.

    (ii) α-Methylnylation of ketones using $Me_2N{=}CH_2^{\oplus}\ I^{\ominus}$.

25. What are (i) Barton ; (ii) Norrish Type I ; and (iii) Norrish Type II photochemical reactions ? Explain their mechanisms with examples.

26. Write an account of reductions using LAH.

27. Discuss the reduction of α, β-unsaturated ketones with $NaBH_4$ (i) In the absence ; and (ii) In the presence of $CeCl_3$.

(6 × 6 = 36 marks)

Section D

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

28. Discuss the major reactions of carbon free radicals.

29. (a) Write an account of optically active non-carbon chiral centers. Illustrate your answer with specific examples.

    (b) Write a brief note on conformations of fused ring and bridged systems.

30. Discuss briefly :

    (i) Bio and chemiluminescence reactions ;

    (ii) Di-π methane rearrangement ; and

    (iii) Sun light induced photoreactions in the atmosphere. (4 + 3 + 3 = 10 marks)

31. Describe (i) The hydroxylation of alkenes ; (ii) Swern oxidation ; and (iii) Muffat oxidation.

(4 + 3 + 3 = 10 marks)

[2 × 10 = 20 marks]

D 93542 **(Pages : 4)** **Name**.....

Reg. No.....

FIRST SEMESTER P.G. DEGREE EXAMINATION, NOVEMBER 2020

(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. Which of the following +3 ion has half-filled sub-shell ?

   a) La. b) Lu.

   c) Ac. d) Gd.

2. Which among the following hydroxides, shows highest solubility in hot and concentrated aqueous NaOH ?

   a) $Lu(OH)_3$. b) $La(OH)_3$.

   c) $Sm(OH)_3$. d) $Nd(OH)_3$.

3. How many bridging and terminal carbonyl groups respectively are present in $Co_4(CO)_{12}$ at low temperature ?

   a) 3 and 9. b) 4 and 6.

   c) 4 and 8. d) 0 and 12.

4. Total electron count in $[Fe_4C(CO)_{12}]^{2-}$ is ————————.

   a) 54. b) 60.

   c) 62. d) 64.

5. On hydrolysis, borazine gives ————————.

   a) Diborane. b) Boric acid.

   c) Tetraborane(10). d) Boron nitride.

Turn over

6. The correct classification of $[B_2H_5]^{2-}$, B_5H_9 and B_5H_{11} respectively is ————————.

a) Closo, arachno, nido.
b) Arachno, closo, nido.
c) Closo, nido, arachno.
d) Nido, arachno, closo.

7. Carbon nanotube is composed entirely by ———————— bonds.

a) sp.
b) sp^2.
c) sp and sp^2.
d) sp, sp^2 and sp^3.

8. The method of synthesis of nanomaterial is ————————.

a) Sol-gel process.
b) Electrodeposition.
c) Sputtering technique.
d) All the above.

9. Conjugate acids of NH_2^- is ————————.

a) NH_3.
b) NH_4OH.
c) NH_4^+.
d) N_2H_4.

10. How many geometrical isomers are possible for a square planar complex with formula $[M_{abcd}]$?

a) 2.
b) 3
c) 4.
d) Geometrical isomerism not possible.

11. According to crystal field theory, Ni^{2+} has two unpaired electron in ————————.

a) Octahedral geometry.
b) Square planar geometry.
c) Tetrahedral geometry.
d) Both octahedral and tetrahedral geometry.

12. Among the following complex species, which one shows optical isomerism ?

a) $[Ni(CN)_4]^{2-}$.
b) $[Pt(NH_3)_4]^{2+}$.
c) $[Ni(CO)_4]$.
d) $[Co(en)_3]^{3+}$ (en=ethylenediamine).

(12 × 1 = 12 marks)

Section B

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

13. What is NMR shift reagent ?

14. What are the factors that favour the formation of metal-metal bonds ?

15. How is polythiazyl prepared ? Why it is called 'one dimensional' metal ?

16. How do fullerenes differ from carbon nanotubes ?

17. Differentiate between kinetic stability and thermodynamic stability of metal complexes.

18. Which is more stable ; $[Cu(en)_2(H_2O)_2]^{2+}$ or $[Cu(en)_3]^{2+}$? Substantiate your answer, (en = ethylenediamine).

(6 × 2 = 12 marks)

Section C

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

19. Compare the differences between 4f and 5f orbitals and the consequences of these on the properties of lanthanides and actinides.

20. Explain isolobal concept with suitable examples.

21. Discuss the application of *styx* numbers in the structural investigation of boron hydrides.

22. Give a brief account of the optical properties of nanomaterials.

23. Describe the spectrophotometric method for the determination of stability constant of a metal complex. How the overall stability constant of a metal complex is related to the step-wise stability constants ?

24. Differentiate between spectrochemical series and nephelauxetic series.

25. Give an account of the isopoly and heteropoly anions of Mo and W.

26. Give a brief account of the biomedical applications of magnetic nanoparticles.

27. Write a note on the geometrical and optical isomerism exhibited by octahedral transition metal complexes.

(6 × 6 = 36 marks)

Section D

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

28. a) Describe ion-exchange method for the separation of lanthanides from monazite.

    b) What is lanthanide contraction ? Discuss its consequences.

(5 + 5 = 10 marks)

Turn over

29. a) Describe the synthesis, properties and structure of $(PNCl_2)_3$.

    b) How do chain silicates differ from sheet silicates ? Discuss the consequences of isomorphous substitution on silicates.

(6 + 4 = 10 marks)

30. a) Discuss the HSAB concept of acids and bases. How it is useful in the study of co-ordination compounds ?

    b) Explain Jahn-Teller distortion with suitable examples.

(6 + 4 = 10 marks)

31. What is CFSE ? Discuss the consequences of crystal field splitting on the ionic radii, heat of hydration and lattice energies of bivalent 3d metal ions.

[2 × 10 = 20 marks]

D 93541 (Pages : 4) Name.....

Reg. No.....

FIRST SEMESTER P.G. DEGREE EXAMINATION, NOVEMBER 2020

(CCSS)

Applied Chemistry

ACH 1C 01—QUANTUM CHEMISTRY

(2019 Admissions)

Time : Three Hours Maximum : 80 Marks

Section A

Choose the correct answer :

1. Which of the following is *not* true for photo-electric effect ?

   (a) Kinetic energy of photo electron is independent of the intensity of incident photon.

   (b) Kinetic energy of photo electron depends on the work function of electron in metals.

   (c) Kinetic energy of photo electron is independent of the frequency of incident photon.

   (d) Photo electric effect is observed only if the frequency of incident photon exceeds the frequency corresponding to threshold energy.

2. Which of the following matter waves have highest wavelength ?

   (a) Electron. (b) Proton.

   (c) H_2. (d) Alpha particles.

3. Which of the following are well behaved functions ?

   (a) A sin kx. (b) e^x.

   (c) e^{x^2}. (d) $\sin^{-1}x$.

4. Choose a function that is eigen function of both $\frac{d}{dx}$ and $\frac{d^2}{dx^2}$.

   (a) A sin kx. (b) e^{ix}.

   (c) e^{x^2}. (d) $\log x$.

5. The energy of a particle in a cubical box of length a is $\frac{14h^2}{8ma^2}$. The degeneracy of the level is :

   (a) 1. (b) 3.

   (c) 6. (d) 8.

6. A particle is confined to one dimensional box of length a. The wave function is $\sqrt{\frac{2}{a}}\sin\left(\pi/a\right)x$. The average value of momentum is :

(a) Zero. (b) h.

(c) $\frac{h}{2\pi}$. (d) $\frac{a}{2}$.

7. The Hermite polynomial $H_x(v=1)$ is :

(a) 1. (b) x.

(c) $4x^2-1$. (d) $8x^3-12x$.

8. Degeneracy of a rotor with $l = 3$ is :

(a) 3. (b) 5.

(c) 7. (d) 9.

9. The 1s wave function for H atom is Ne^{-r/a_0}. The probability density for finding electron is maximum at :

(a) $r = 0$. (b) $r = a_0$.

(c) $\frac{2r}{a_0}$. (d) Infinity.

10. According to Pauli principle the total wave function is :

(a) Symmetric. (b) Asymmetric.

(c) Antisymmetric. (d) Cyclic.

11. ———— energy levels converge.

(a) Electronic. (b) Simple harmonic oscillator.

(c) Rotation. (d) Translation.

12. The spectroscopic term symbol for the ground state of C is :

(a) $^3P_3$. (b) $^3P_0$.

(c) $^3S_0$. (d) $^3D_0$.

(12 × 1 = 12 marks)

Section B

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

13. Calculate the uncertainty in momentum for electron confined to one dimensional box of length 10 *nm*.

14. Find the commutator of $\hat{x}$ and $\hat{p}_x$.

15. Write recursion formula. Explain its significance.

16. Define spherical harmonics. Write one example.

17. What do you mean by Polar plots ?

18. State and explain independent particle model.

(6 × 2 = 12 marks)

Section C

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

19. (a) Define Hermitian operator. Show that they have real eigen functions.

    (b) Show that eigen functions of Hermitian operators are mutually orthogonal.

20. Apply Schrödinger wave equation for one dimensional box of length '*a*'. Find eigen functions and eigen values.

21. Find Hermite polynomial $H_x(v=4)$.

22. Apply Schrödinger wave equation for a planar rotor. Find eigen functions and eigen values.

23. Find commutator of $\hat{L}x$ and $\hat{L}y$.

24. Explain the term 'radial probability distribution. Draw radial probability distribution for 1*s* and 2*s* atomic orbitals. Discuss.

25. How do you account for the fine structure of hydrogen spectrum ? Discuss structure of hydrogen spectrum ? Discuss.

26. State and prove variation theorem.

27. What is meant by Slater orbitals. Discuss Slater's rules with one example.

(6 × 6 = 36 marks)

Section D

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

28. Discuss postulates of quantum mechanics.

29. Apply Schrödinger wave equation for a simple harmonic oscillator. Find eigen functions and eigen values.

30. (a) Apply Schrödinger wave equation for H atom. Transform into spherical polar coordinates. Separate the variables.

    (b) Discuss shapes of *d* atomic orbitals.

31. Briefly discuss Hartree Fock self consistent field method of solving many electron atoms.

(2 × 10 = 20 marks)