C 83422 (Pages : 4) Name.....

Reg. No.....

SECOND SEMESTER P.G. DEGREE EXAMINATION, APRIL 2020

(CCSS)

M.Sc. Applied Chemistry

ACH 2C 08—PHYSICAL CHEMISTRY–II

(2019 Admissions)

Time : Three Hours Maximum : 80 Marks

Section A

Choose the correct answer.
Answer **all** *questions.*
Each question carries 1 *mark.*

1. Magnitude of the partition function varies in the order :
   (a) Translation > Rotation > Vibration > Electronic.
   (b) Electronic > Vibration > Rotation > Translation.
   (c) Rotation > Vibration > Translation > Electronic.
   (d) Vibration > Rotation > Translation > Electronic.
2. Degeneracy associated with ortho hydrogen is :
   (a) 1. (b) 2.
   (c) 3. (d) 4.
3. Identify the correct statement :
   (a) Maxwell Boltzman statistics is applicable only at high pressures.
   (b) Maxwell Boltzman statistics is applicable only at low temperatures.
   (c) All particles obey Maxwell Boltzman statistics under dilute system conditions.
   (d) Maxwell Boltzman statistics does not permit multiple occupancy.
4. Which of the following statements is *not* true for Fermi level ?
   (a) It is the highest occupied level at 0K.
   (b) It is located midway between highest filled level and lowest unfilled level.
   (c) It is a measure of potential energy of electrons in metals.
   (d) It depends on the temperature.

5. Non-stoichiometric ZnO is an example for ————.

(a) n-type semiconductor. (b) p-type semiconductor.

(c) Insulator. (d) Conductor.

6. Which of the following statements is *not* true for piezoelectric crystals ?

(a) It must be non-centrosymmetric.

(b) It must be centrosymmetric.

(c) Quartz is an example for piezoelectric crystal.

(d) They find application as transformer.

7. Stern-Volmer equation is associated with :

(a) Photosensitizer. (b) Fluorescence quenching.

(c) Jablonski diagram. (d) Chemiluminescence.

8. Which of the following statement is *not* true for solar cells ?

(a) Principle is photovoltaic effect.

(b) Silicon is used in solar cells.

(c) Exertions are generated during working.

(d) It generates heat by absorbing sun light.

9. Which of the following radiation is used in EPR spectroscopy ?

(a) Radiofrequency. (b) Microwave.

(c) X-rays. (d) Gamma rays.

10. In FTIR ———— is used.

(a) Interferometer. (b) Grating.

(c) Wavelength selector. (d) Photo cell.

11. Which of the following nuclei is NMR inactive :

(a) ^{14}N. (b) ^{28}Si.

(c) ^{17}O. (d) ^{23}Na.

12. Number of lines in the EPR spectrum of naphthalene negative ion is :

(a) 1. (b) 3.

(c) 8. (d) 25.

(12 × 1 = 12 marks)

Section B

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

13. Rationalise third law of thermodynamics using statistical concepts.
14. Find Characteristic temperature of a solid with vibrational frequency 3000 cm^{-1}.
15. Distinguish between ferromagnetism and anti-ferromagnetism with one example for each.
16. Distinguish between E-type and P-type phosphorescence.
17. Find the frequency for J = 9 —> 10 transition rotational constant B = 10 cm^{-1}.
18. A set of protons absorbs at a frequency 900 Hz downfield with respect to TMS in a 300 MHz NMR instrument. Calculate chemical shift (δ).

(6 × 2 = 12 marks)

Section C

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

19. Define partition function. Derive equations to show its relationship with (a) internal energy ; (b) entropy.
20. How would you calculate equilibrium constant theoretically ? Discuss.
21. Calculate heat capacity of diamond at 1000 K. Its characteristic temperature 1860 K.
22. Show that all particles follow Maxwell Boltzman statistics under dilute system condition.
23. What is Meissner effect ? Discuss.
24. Br_2 undergoes photodissociation using 435.8 nm radiation. 0.075 milli inches of B_2 dissociated during exposure of 1105 sec with light intensity of 1.4×10^{-3} Js^{-1}. The solution absorbed 80.1 % of light passing through it. Calculate the quantum field.
25. Find the value of rotational quantum number J at which maximum intensity is observed for a diatomic molecule with rotation constant B = 10 cm^{-1}. Temperature is 25°C in the microwave spectrum.
26. In the IR spectrum of HCl fundamental absorption and first overtone are observed at 2886 and 5668 cm^{-1} respectively. Find the fundamental vibration frequency, anharmonicity constant and force constant.
27. How many lines are observed in the EPR spectrum of ND_3 (radical). What is the relative intensity ? Justify your answer.

(6 × 6 = 36 marks)

Turn over

Section D

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

28. (a) Derive Boltzan exponential law.

    (b) Find the ratio of population at 25°C for energy levels separated by 100 cm^{-1}. The ground state is non-degenerate. Excited state is triply degenerate. T = 300 K.

29. Write virial equation of state. Evaluate second virial co-efficient.

30. Briefly discuss theories of super conductivity.

31. Briefly discuss theory of FTNMR.

(2 × 10 = 20 marks)

SECOND SEMESTER P.G. DEGREE EXAMINATION, APRIL 2020

(CCSS)

M.Sc. Applied Chemistry

ACH 2C 07—ORGANIC CHEMISTRY–II

(2019 Admissions)

Time : Three Hours Maximum : 80 Marks

Section A

Answer **all** *questions.*

Each question carries 1 *mark.*

1. The reaction of the enolate of diethyl malonate with cyclohex-2-en-1 -one will lead to ————.

   (a) C-C bond formation at C3 carbon atom of cyclohex-2-en-1-one.

   (b) C-C bond formation at C2 carbon atom of cyclohex-2-en-1-one.

   (c) C-C bond formation at C1 carbon atom of cyclohex-2-en-1-one.

   (d) C-C bond formation at C6 carbon atom of cyclohex-2-en-1-one.

2. When 2-methylcyclohexanone is treated with ————, the preferred enolate formation will involve the hydrogen on ring carbon atom numbered ————.

   (a) NaOEt, EtOH, 25°C ; C2. (b) LDA, THF, –78°C ; C2.

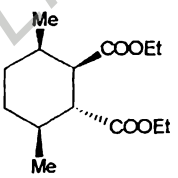
   (c) LDA, THF, –78°C ; C6. (d) NaOEt, EtOH, 25°C ; C6.

3. E, E- 2, 4-hexadiene would form by heating ————.

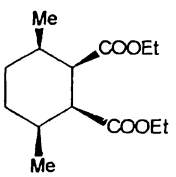
   (a) E, Z - 2, 4-hexadiene. (b) 1,2- dimethylcyclobutene.

   (c) Z - 3, 4-dimethylcyclobutene. (d) E-3, 4-dimethylcyclobutene.

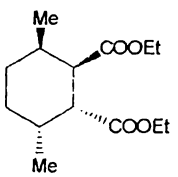
4. The 1, 4-cycloaddition of E, E-hexa-2, 4-diene with E-EtOCO-CH=CH-COOEt gives ————.



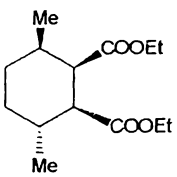
A



B



C



D

   (a) A. (b) B.

   (c) C. (d) D.

Turn over

5. Shapiro reaction of acetophenone, and using MeBr as the alkyl halide, leads to ————.

   (a) $PhCO\text{-}CH_2Me$. (b) $PhCH{=}CMe_2$.

   (c) PhCH=CHMe. (d) $Ph(Me)C{=}CH_2$.

6. Hofmann-Lofler-Frytag reaction involves ———— of a ————.

   (a) Heterolytic fission ; N-halogen bond.

   (b) Homolytic fission ; N-halogen bond.

   (c) Homolytic fission ; C-halogen bond.

   (d) Homolytic fission ; N-hydrogen bond.

7. Monomers for cationic polymerizations are generally ————.

   (a) Alkenes with electron donating substituents.

   (b) Alkenes with electron withdrawing substituents.

   (c) Alkenes with either electron donating or withdrawing substituents.

   (d) Alkenes that carry no electron donating or withdrawing substituents.

8. Amorphous polymers can best be distinguished from other polymers by ————.

   (a) Thermogravimetry. (b) X-ray diffraction.

   (c) Electron diffraction. (d) X-ray and /or electron diffraction.

9. Under Bamberger rearrangement conditions, Ph-NHOH forms ———— as an intermediate.

   (a) $PhN^{\oplus}H$. (b) PhN.

   (c) $PhN^{\ominus}H$. (d) $PhNH_2$.

10. ———— can undergo Stieglitz rearrangement.

    (a) PhNHOH. (b) $Ph_3C\text{-}NHOH$.

    (c) $PhNHNH_2$. (d) $Ph_3C\text{-}NHNH_2$.

11. Vilsmeier-Haack reaction of pyrrole using DMF gives ————.

    (a) Pyrrole-3-carbaldehyde. (b) 2-acetylpyrrole.

    (c) Dipyrrolylmethane. (d) pyrrole-2-carbaldehyde.

12. 2-Aminobenzylamine upon reaction with HCOOH followed by oxidation affords ————.

    (a) Isoquinoline. (b) Quinazoline.

    (c) Quinoline. (d) Benzimidazole.

(12 × 1 = 12 marks)

Section B

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

13. Suggest a method for the synthesis of Me_2N-CH_2-CH(Me)-CO-CH_2Me by a reaction based upon carbonyl group reactivity. Write the mechanism.

14. The compound Ph-O-CH_2CH=$CHCH_3$ undergoes isomerisation upon mild heating. Identify the product and explain its formation.

15. Ramberg-Bäcklund reaction is thought to involve a cyclic intermediate. Illustrate its formation and its further reaction with a typical example.

16. What is co-ordination polymerization ?

17. Compound A rearranges to 4-aminophenol upon heating with strong aq. sulphuric acid. Identify A and write the mechanism.

18. What are oxazines ? Write their structures.

(6 × 2 = 12 marks)

Section C

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

19. Explain the formation of enamines. Illustrate their use in alkylation reactions.

20. Predict the products in the NaOEt promoted reactions, followed by aq. acidic work up, of compounds A and B respectively. Explain their formation.

    (A) $CH_2(CH_2$-CH_2-$COOMe)_2$.

    (B) CH_3CH_2-COOMe.

21. Establish the selection rules for [4 + 2] cycloadditions using FMO approach.

22. Write the mechanism and synthetic use of Hayashi reaction and Julia olefination.

23. Discuss the mechanism of : (i) Shapiro reaction ; and (ii) Peterson reaction.

24. What are the factors that influence glass transition temperature of polymers ?

25. Explain with mechanism the evolution of nitrogen gas during von Richter rearrangement.

26. Illustrate with examples intermolecular group migration during rearrangement reactions from nitrogen to carbon centres.

27. How can benzothiophen be synthesized ? What are its major reactions ?

(6 × 6 = 36 marks)

Turn over

Section D

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

28. Elucidate the selection rules governing thermal and photochemical [1, 3] and [1, 5] suprafacial and antarafacial sigmatropic rearrangements based on FMO treatment.

29. (a) Define the molecular weights of polymers and describe their determination.

    (b) Describe the tacticity of polymers with specific examples.

(5 + 5 = 10 marks)

30. Write the mechanism of Michael reaction, cheletropic reaction and Sharpless asymmetric epoxidation.

(3 + 3 + 4 = 10 marks)

31. Describe the general synthetic methods available for preparing pyrrole, imidazole, pyrimidine and isoquinoline systems.

(2 + 2 + 3 + 3 = 10 marks)
[2 × 10 = 20 marks]

C 83420 (Pages : 4) Name.....

Reg. No.....

SECOND SEMESTER P.G. DEGREE EXAMINATION, APRIL 2020

(CCSS)

M.Sc. Applied Chemistry

ACH 2C 06—INORGANIC CHEMISTRY—II

(2019 Admissions)

Time : Three Hours Maximum : 80 Marks

Section A

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

1. The number of microstates possible for p^2 electronic configuration is ————————.

   (a) 8. (b) 10.

   (c) 15. (d) 18.

2. Crystal field stabilization energy value for $[Ti(H_2O)_6]^{3+}$ that has an absorption maximum at 492 nm is ————————.

   (a) 20325 cm^{-1}. (b) 12195 cm^{-1}.

   (c) 10162 cm^{-1} (d) 8130 cm^{-1}.

3. Which of the following free ions has the lowest magnetic moment ?

   (a) Ce^{3+}. (b) Nd^{3+}.

   (c) Sm^{3+}. (d) Gd^{3+}.

4. The compound that both paramagnetic and coloured is ————————.

   (a) $K_2Cr_2O_7$. (b) $(NH_4)_2[TiCl_6]$.

   (c) $VOSO_4$. (d) $K_3[Cu(CN)_6]$.

5. The reaction of $[PtCl_4]^{2-}$ with NH_3 give rise to the formation of ————————.

   (a) $[PtCl_4(NH_3)_2]^{2-}$. (b) *trans*-$[PtCl_2(NH_3)_2]$.

   (c) $[PtCl_2(NH_3)_4]$. (d) *cis*-$[PtCl_2(NH_3)_2]$.

4 over

6. Designate the following complexes x, y & z as inert or labile :

$x = [Al(C_2O_4)_3]^{3-}$ $y = [V(H_2O)_6]^{2+}$ $z = [Cr(C_2O_4)_3]^{3-}$

(a) x is labile, y and z are inert. (b) x and y are inert, z is.

(c) x is inert, y and z are labile. (d) x and y are labile, y is inert.

7. The reaction,

$$\left[Co\left(H_2O\right)_5 Cl\right]^{2+} + \left[Cr\left(H_2O\right)_6\right]^{2+} \rightarrow \left[Co\left(H_2O\right)_6\right]^{2+} + \left[Cr\left(H_2O\right)_5 Cl\right]^{2+}$$ occurs through :

(a) Complementary electron transfer reaction.

(b) Inner-sphere electron transfer reaction.

(c) Non-complementary electron transfer reaction.

(d) Outer-sphere electron transfer reaction.

8. The electron transfer reaction between $[Co(NH_3)_5Cl]^{2+}$ and $[Cr(H_2O)_6]^{2+}$ in acidic medium leads to the formation of ————————.

(a) $[Cr(NH_3)_5(H_2O)]^{2+}$. (b) $[Cr(NH_3)_5Cl]^{2+}$.

(c) $[Cr(H_2O)_5Cl]^{2+}$. (d) $[Co(NH_3)_6]^{3+}$.

9. The complex which obey the 18-electron rule is ————————.

(a) $Fe(CO)_4$. (b) $Cr(CO)_5$.

(c) $Cr(\eta^5\text{-}C_5H_5)_2$. (d) $Ni(CO)_3(P\ Ph_3)$.

10. Among the following statements, which statement is false about ferrocene ?

(a) It obeys 18-electron rule. (b) It is diamagnetic.

(c) It's colour is orange red. (d) It resists electrophilic substitution.

11. Oxidative addition and reductive elimination steps are favoured by ————————.

(a) Electron rich metal clusters.

(b) Electron deficient metal centres.

(c) Electron rich and electron deficient metal centres respectively.

(d) Electron deficient and electron rich metal centres respectively.

12. In hydroformylation reaction using $[Rh(P\ Ph_3)_3(CO)H]$ as the catalyst, addition of excess P Ph_3 could ————————.

(a) Increase the reaction. (b) Decrease the rate of reaction.

(c) Not influence the rate of reaction. (d) Stop the reaction.

(12 × 1 = 12 marks)

Section B

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

13. Differentiate between microstate and atomic state.

14. What is meant by TIP ?

15. The rate constant for hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ in basic solution is million times greater than that found for acidic solutions ; why ?

16. What is bridging group effect in inner-sphere electron transfer reactions ? Explain with an example.

17. What hapticities are possible for $C_5H_5^-$ towards a metal ion ? Sketch the interactions.

18. Explain the role of metal complexes in enantioselective synthesis with examples.

(6 × 2 = 12 marks)

Section C

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

19. Which electronic transition would you expect to be more intense ; $^3A_{2g} \rightarrow {}^3T_{2g}$ in a nickel(II) octahedral or $^3Ti \rightarrow {}^3T_2$ in nickel(II) tetrahedral complex ? Give reasons. Assign the other d-d transitions observed for nickel(II) in its octahedral complexes.

20. Explain the different ferro and antiferromagnetic exchange pathways with suitable examples. What is meant by spin crossover system ?

21. Explain template effect with suitable examples.

22. How Marcus theory connects thermodynamics and kinetics for outer sphere reactions in metal complexes ?

23. What are fluxional organometallic compounds ? How NMR spectroscopy is useful in the structural investigation of such compounds ?

24. Explain the different bonding modes of NO towards metal ions in metal nitrosyl complexes. How IR spectroscopy can be used to identify these bonding modes ?

25. Write a note on the magnetic properties of f-block elements.

26. What are the distinguishing features of inner sphere and outer sphere redox reactions ?

27. State and explain 16- and 18- electron rules as applied to organometallic compounds, giving examples.

(6 × 6 = 36 marks)

Section D

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

28. What are the different types of electronic transitions which give rise to the spectra of transition metal complexes ? Explain the selection rules for the electronic spectra of metal complexes and the relaxation of these selection rules and also reasons for broadening of the absorption spectral bands.

29. What is trans effect ? Explain its theories and any *two* synthetic applications.

30. How is ferrocene prepared ? Give an account of its stability, important reactions and structural features.

31. Describe the application of organometallic catalysts in hydrogenation, hydroformylation and isomerization of alkenes, bringing out the mechanisms involved.

(2 × 10 = 20 marks)

C 83419 (Pages : 4) Name.....

Reg. No.....

SECOND SEMESTER P.G. DEGREE EXAMINATION, APRIL 2020

(CCSS)

M.Sc. Applied Chemistry

ACH 2C 05—GROUP THEORY AND CHEMICAL BONDING

(2019 Admissions)

Time : Three Hours Maximum : 80 Marks

Section A

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

Choose the correct answer :

1. H_2O_2 belongs to ——— point group.

   (a) c_2. (b) c_{2v}.

   (c) c_{2h}. (d) $D \propto h$.

2. Inverse of s_3 is :

   (a) s_3^2. (b) s_3^3.

   (c) s_3^5. (d) s_3^6.

3. Choose the correct statement :

   (a) A point group has any number of reducible representation.

   (b) A point group has fixed number of reducible representation.

   (c) A point group has any number of irreducible representation.

   (d) The number of irreducible representation of a group is equal to the order of the group.

4. Which of the following is *not* true for A_{2g}.

   (a) It has inversion center.

   (b) The character under c_n (Principal axes) is – 1.

   (c) It is symmetric with respect to σ_h.

   (d) It is an one dimensional representation.

5. In the gamma cart for ethylene (D_{2h}) the character of the matrix representing E is :

   (a) 1. (b) 3.

   (c) 9. (d) 18.

6. Mutual exclusion principle is applicable to :

   (a) XeF_4. (b) $XeOF_4$.

   (c) PCl_3. (d) CH_2Cl_2.

7. The number of π (pi) electrons in c_2 is :

   (a) 0. (b) 2.

   (c) 3. (d) 4.

8. The spectroscopic term symbol for ground state of O_2^- is :

   (a) $^2\pi_g$. (b) $^2\pi_u$.

   (c) $^2\Sigma_g^+$. (d) $^2\Sigma_g^-$.

9. Delocalization energy of benzene is :

   (a) 8 β. (b) 6 β.

   (c) 4 β. (d) 2 β.

10. Which of the following statements is true for Lennard Jone's Potential ?

   (a) It is also known as 12 – 6 potential.

   (b) It is also known as 6 – 6 potential.

   (c) It takes into account attractive interaction only.

   (d) It is Independent of molecular parameters.

11. Which of the following transitions is allowed ?

   (a) $^2\Sigma_g^+ \rightarrow {}^2\Sigma_g^-$. (b) $^2\Sigma_g^+ \rightarrow {}^3\Sigma_g^+$.

   (c) $^2\Sigma_g^+ \rightarrow {}^2\pi_u$. (d) $^2\Sigma_g^+ \rightarrow {}^2\Delta_g$.

12. Projection open $\hat{P}_{A_2}$ for c_{2v} is :

   (a) $IE + 1c_{2z} + 1\sigma_{vxz} + 1\sigma'_{vyz}$. (b) $IE + 1c_{2z} - 1\sigma_{vxz} - 1\sigma'_{vyz}$.

   (c) $IE - 1c_{2z} + 1\sigma_{vxz} - 1\sigma'_{vyz}$. (d) $IE - 1c_{2z} - 1\sigma_{vxz} + 1\sigma'_{vyz}$.

(12 × 1 = 12 marks)

Section B

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

13. Generate matrices for :

    (a) c_4. (b) s_3.

14. Find the similarity transform of any *one* of the vertical planes in NH_3 (c_{3v}).

15. Rationalise mutual exclusion principle using group theory.

16. Write trial function for H_2 using MO theory. Justify your answer.

17. State and explain non-crossing rule.

18. Distinguish between SAGO and SALC.

(6 × 2 = 12 marks)

Section C

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

19. Using Great Orthogonality Theorem (GOT) derive c_{4v} character table.

20. List the symmetry operations possible on D_{4h}. Classify them into different classes.

21. Derive reduction formula using GOT.

22. Taking the positional co-ordinates of all the atoms in cis-butadiene (c_{2v}) generate a reducible representation. Reduce it into its IR components.

23. Discuss bonding in H_2O using MO theory.

24. The π (*pi*) molecular orbitals of cis-butadiene are given. Find the free valence around each carbon atom.

$$\Phi_1 = 0.372p_1 + 0.602p_2 + 0.602p_3 + 0.372p_4.$$

$$\Phi_2 = 0.602p_1 + 0.372p_2 - 0.372p_3 - 0.602p_4.$$

$$\Phi_3 = 0.602p_1 - 0.372p_2 - 0.372p_3 + 0.602p_4.$$

$$\Phi_4 = 0.372p_1 - 0.602p_2 + 0.602p_3 - 0.372p_4.$$

25. Predict the allowed electronic transitions in carbonyl group. Use c_{2v} character table.

26. Find the π (*pi*) molecular orbitals and corresponding energies for allyl cation using HMO method.

27. Write a brief account of the quantum mechanical treatment of intermolecular forces.

(6 × 6 = 36 marks)

Section D

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

28. Find IR and Raman active vibrations of NH_3. (c_{3v}).
29. Discuss bonding in H_2 using VB theory.
30. Find the hybridized orbitals of B in BF_3 (D_{3h}).
31. Discuss briefly :
    (a) Correlation diagram.
    (b) Frost Hückel circle mnemonic devices.
    (c) Transition moment integral.

c_{2v}	E	c_{2z}	σ_{vxz}	σ'_{vyz}		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	− 1	− 1	Rz	xy
B_1	1	− 1	1	− 1	x, Ry	xz
B_2	1	− 1	− 1	1	y, Rx	yz

c_{3v}	E	$2c_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	− 1	Rz	
E	2	− 1	0	(x, y) (R_x, R_y)	$(x^2 - y^2, xy)$ (xz, yz)

D_{3h}	E	$2c_3$	$3c_2$	σh	$2s_3$	$3\sigma_d$		
A'_1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A'_2	1	1	− 1	1	1	− 1	Rz	
E'	2	− 1	0	2	− 1	0	(x, y)	$(x^2 - y^2, xy)$
A''_1	1	1	1	− 1	− 1	− 1		
A''_2	1	1	− 1	− 1	− 1	1	z	
E''	2	− 1	0	− 2	1	0	(R_x, R_y)	(xz, yz)

(2 × 10 = 20 marks)

C 83418 (Pages : 4) Name.....

Reg. No.....

SECOND SEMESTER P.G. DEGREE EXAMINATION, APRIL 2020

(CCSS)

M.Sc. Applied Chemistry

ACH 2C 11—PHYSICAL CHEMISTRY—II

(2015 Admissions)

Time : Three Hours Maximum : 80 Marks

Section A

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

Choose the correct answer :

1. Which of the following is *not* a boson ?

   (a) Photons. (b) He atom.

   (c) N atom. (d) Deuterium.

2. Choose the correct statement :

   (a) Ortho : Para ratio of hydrogen is 1 : 3.

   (b) In ortho hydrogen only even J States are occupied.

   (c) In Para hydrogen only even J States are occupied.

   (d) In ortho hydrogen all J States are occupied according to Boltzmann exponential law.

3. Diamond has very high characteristic temperature because of :

   (a) Strong bonding. (b) Low atomic mass.

   (c) Low force constant. (d) (a) and (b).

4. Helium shows Bose Einstein condensation at very low temperature and high pressures because :

   (a) It obeys dilute system condition.

   (b) It does not obey dilute system condition.

   (c) It obeys Maxwell-Boltzmann statistics.

   (d) It attains triple point.

Turn over

5. Which of the following is *not* true for Fermi level of a metal ?

   (a) It is the highest occupied level at OK.

   (b) Its location is mid-way between highest occupied level and lowest unoccupied level.

   (c) It is shifted by change in electron density of the d-band.

   (d) It is independent of the electron density of d-band.

6. Which of the following is a conducting polymer ?

   (a) Polyaniline. (b) Polyethylene.

   (c) Polyvinyl chloride. (d) Zeolite.

7. Which of the following photochemical reaction has highest quantum yield ?

   (a) $H_2 + Cl_2$. (b) $H_2 + Br_2$.

   (c) $H_2 + I_2$. (d) $O_2 + O$.

8. The color centers in alkali halides are due to :

   (a) Trapped electrons. (b) Dopped transition metals.

   (c) Cation excess. (d) Anion excess.

9. The distance between the first lines in stokes and antistokes region of Rotational Raman Spectrum is :

   (a) 2B. (b) 4B.

   (c) 6B. (d) 12B.

10. A solution shows absorbance A = 2.0. The % radiation absorbed in :

    (a) 50. (b) 90.

    (c) 99. (d) 100.

11. A set of protons showed resonance absorption 900 Hz lower w.r.t. TMS in 300 MHz NMR instrument. The chemical shift δ is :

    (a) – 3. (b) 0.

    (c) 3. (d) 9.

12. An EPR signal is split into ———— lines due to zero field splitting in d^3 system.

    (a) 2. (b) 3.

    (c) 4. (d) 6.

(12 × 1 = 12 marks)

Section B

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

13. Show that $P\overline{V} = RT$ for an ideal gas using partition functions.

14. Explain term 'Gas Degeneration'.

15. Distinguish between Type I and Type II Superconductors with examples.

16. Explain with example 'Chemiluminescence'.

17. Explain the term 'Resonance Raman line'.

18. State and explain Mc Connell equation.

(6 × 2 = 12 marks)

Section C

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

19. Derive an equation for vibrational partition function. Write equation for vibrational partition function of a polyatomic molecule with frequencies r_1, r_2 and r_3.

20. Calculate the temperature at which 10 % molecules are in the first excited state if it is 400 KJ mol^{-1} above the ground state. The ground state is non-degenerate and excited state in triply degenerate.

21. Calculate heat capacity of diamond at 1000 K. Its characteristic temperature is 1860 K.

22. Briefly explain the working of a solar cell.

23. Discuss the working of a two stage laser.

24. Write Morse equation. Represent graphically. Show that real molecules approximate to simple harmonic oscillator at low amplitude vibration.

25. What are the drawbacks of dispersive IR ? How are they overcome by FT ? Discuss.

26. What are the contributing factors to spin-spin splitting ? Discuss.

27. State Karplus relationship. Discuss.

(6 × 6 = 36 marks)

Turn over

Section D

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

28. (a) Discuss anomalous heat capacity of H_2.

    (b) Calculate rotational partition function for CO. Its bond length is 1.13 Å. T = 300 K.

29. Write virial equation of state. Evaluate the second term in the equation.

30. Discuss briefly Kinetics of :

    (a) Photo Polymerization.

    (b) Photolysis of ammonia.

31. How is nuclear magnetic resonance produced ? Discuss.

(2 × 10 = 20 marks)

SECOND SEMESTER P.G. DEGREE EXAMINATION, APRIL 2020

(CCSS)

M.Sc. Applied Chemistry

ACH 2C 08—GROUP THEORY AND CHEMICAL BONDING

(2015 Admissions)

Time : Three Hours Maximum : 80 Marks

Section A

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

1. The symmetry operation, C_6^2 =

   (a) E. (b) S_3.

   (c) C_3. (d) *i*.

2. The order of D_2h point group is :

   (a) 4. (b) 3.

   (c) 2. (d) 8.

3. Mulliken symbol A1 or $A1_g$ corresponds to :

   (a) 2-D representation.

   (b) 1-D representation symmetric only with respect to principal rotation.

   (c) Totally symmetric irreducible representation.

   (d) 1-D representation antisymmetric with respect to inversion.

4. The characters of the irreducible representations of the elements forming a class :

   (a) Remains the same. (b) Changes the sign.

   (c) Orthogonal to each other. (d) None of the above.

5. The number of molecular vibrations in NH_3 is :

   (a) 5. (b) 7.

   (c) 8. (d) 6.

12. What is the electron-pair geometry of the central oxygen atom of ozone (O_3) ?

(a) Linear. (b) Trigonal bipyramidal.

(c) Tetrahedral. (d) Trigonal planar.

(12 × 1 = 12 marks)

Section B

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

13. What are the conventions followed in fixing the principal axis of a molecule ?

14. Write down the matrix representation of $C_2(y)$ symmetry operation.

15. What are overlap integrals ?

16. What is Born-Oppenheimer approximation ? Explain its significance in solving molecular Schrödinger equation.

17. Draw the Frost circle mnemonic for cyclobutadiene and interpret.

18. What is transition moment integral ? State its significance.

(6 × 2 = 12 marks)

Section C

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

19. Draw the geometries of the following molecules, their symmetry elements and assign the point group :

(a) CH_2Cl_2 (b) Allene.

20. Construct a representation for P_z orbital on the oxygen atom of H_2O.

21. Explain Great Orthogonality theorem with all the important rules derived from it.

22. Construct a group multiplication table for C_{3V}.

23. Explain in detail various intermolecular interactions with equations.

24. Explain the valence bond approach in determining the bonding in H_2 molecule.

25. Construct the MO diagram for CO, O_2, and O_2^+. Discuss their stability based on bond order.

26. Derive the various spectroscopic term symbols of carbon molecule and arrange them in the order of their energies.

27. What are the salient features of VSEPR theory ? Write down its advantages and limitations.

(6 × 6 = 36 marks)

Section D

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

28. Derive the energy equation for H_2 molecule on the basis of molecular orbital theory and show that the error in calculated value of energy is about 56% compared to the experimental value.

29. (a) Apply the Great Orthogonality Theorem to construct the character table for C_{4V} point group.

(b) Decompose the following reducible representations of the C_{4V} point group :

	E	$2C_4$	C_2	$2\sigma_V$	$2\sigma_d$
$\Gamma 1$	11	1	– 1	5	1
$\Gamma 2$	6	0	2	0	0

(6 + 4 = 10 marks)

30. Using group theory, obtain the selection rules for vibrational transitions in IR and Raman spectroscopy. Examine the IR and Raman activities of the vibrations of the water molecule.

31. (a) Briefly explain the approximations involved in the Hückel MO method.

(b) Calculate the delocalization energy of benzene using HMO method.

(8 + 2 = 10 marks)

[2 × 10 = 20 marks]

C 3928 (Pages : 4) Name.....

Reg. No.....

SECOND SEMESTER P.G. DEGREE EXAMINATION, APRIL 2021

(CCSS)

Applied Chemistry

ACH 2C 08—PHYSICAL CHEMISTRY – II

(2019 Admissions)

Time : Three Hours Maximum : 80 Marks

Section A

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

Choose the correct answer :

1. How many ways you can arrange two distinguishable particles A and B in three equivalent boxes without any restriction on the number of particles in each box ?

   (a) 3. (b) 6.

   (c) 8. (d) 9.

2. Which of the following partition functions has highest magnitude ?

   (a) Translation. (b) Rotation.

   (c) Vibration. (d) Electronic.

3. Identify the wrong statement about heat capacity of solids :

   (a) Molar heat capacity of monoatomic solids attains a lining value of 3R at very high temperature.

   (b) Einstein theory assumes a single frequency.

   (c) Einstein's theory is valid for all temperatures

   (d) Debye's theory is valid for all temperatures.

4. Identify the correct statement regarding Bose-Einstein condensation :

   (a) It is valid only for the He and few other bosons.

   (b) It is applicable only for electrons.

   (c) It is valid for all bosons.

   (d) It is valid for all particles.

5. Identify by the correct statement about ZnO semiconductor :

   (a) It is cation deficient.

   (b) It is anion deficient.

   (c) Zn atoms occupy interstitial positions.

   (d) 4S atomic orbital of Zn slightly below the conduction band of ZnO.

6. Identify the wrong statement regarding zeolites :

   (a) The word meaning is boiling stone.

   (b) They are aluminosilicates.

   (c) They are mesoporous materials.

   (d) They show shape selectivity.

7. One Einstein in photochemistry means :

   (a) Energy of one photon.

   (b) Energy of one Avagadro number of photons.

   (c) One Avagadro number of photons.

   (d) Energy of one Avagadro number of electrons.

8. Photochemical reaction of H2 with ———— has highest quantum yield.

   (a) F_2. (b) Cl_2.

   (c) Br_2. (d) I_2.

9. Nonradiative deexcitation of ———— levels is made use of in microwave ovens.

   (a) Electronic. (b) Vibration.

   (c) Rotation. (d) Translation.

10. In Raman spectroscopy ———— radiation is analysed.

   (a) Absorbed. (b) Emitted.

   (c) Elastically scattered. (d) Inelastically scattered.

11. In a 300 MHz NMR instrument δ and J for a particular set of protons is 3.0 and 5.2 which of the following statements is true ?

   (a) Both δ and J are field dependent.

   (b) Both δ and J are field independent.

   (c) δ is field dependent J is field independent.

   (d) δ is field independent, J is field dependent.

12. Kramer's theorem deals with ———— coupling.

(a) Proton-proton. (b) Proton-electron.

(c) Electron-electron. (d) None of these.

(12 × 1 = 12 marks)

Section B

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

13. Distinguish between microstate and macrostate with examples.
14. Define Fermi level. Explain its significance.
15. What is Hall effect ?
16. State and explain laws of photochemistry.
17. Account for the Q branch of NO.
18. Define Gynomagnetic ratio. Explain its significance.

(6 × 2 = 12 marks)

Section C

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

19. (a) Derive Sackur-Jetrode equation.

(b) Calculate absolute entropy of He at 1 atmosphere pressure and 0°C.

20. Briefly discuss anomalous heat capacity of molecular hydrogen.
21. Derive Fermi Dirac distribution law.
22. Define piezo electricity. Discuss its applications.
23. Derive Stern–Volmer equation.
24. Discuss Doppler broadening.
25. How would you determine dipole moment of a linear molecule using microwave spectroscopy ? Discuss.
26. Calculate the magnetic field at which protons resonate with radiation of frequency 400 MHz. $I_N = 5.585$, $\mu_N = 5.05 \times 10^{-27} JT^{-1}$.
27. Discuss the mechanisms of hyper fine interaction in EPR spectroscopy.

(6 × 6 = 36 marks)

Section D

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

28. Discuss Dehye's theory of heat capacity of solids.

29. Briefly discuss Bose Einstein condensation.

30. Discuss band theory of solids.

31. Write mechanism of photochemical reaction between H_2 and Cl_2. Derive the rate law.

(2 × 10 = 20 marks)

C 3927 (Pages : 4) Name.....

Reg. No.....

SECOND SEMESTER P.G. DEGREE EXAMINATION, APRIL 2021

(CCSS)

Applied Chemistry

ACH 2C 07—ORGANIC CHEMISTRY—II

(2019 Admissions)

Time : Three Hours Maximum : 80 Marks

Section A

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

1. To form a kinetic enolate from an unsymmetrical aliphatic ketone, it is best treated with ——— at ———.

   (a) $NaNH_2$ in dry EtOH ; – 10°C.

   (b) Li (– $NCHMe_2)_2$ in THF : – 78°C.

   (c) Na OCH_2CH_3, Ethanol ; – 78°C.

   (d) Na OCH_2CH_3, Ethanol ; 25°C.

2. Among compounds A-D given below, ——— may NOT add the anion of nitromethane in a 1,4-addition.

   A. Me–CO–CH=CH_2. B. MeO–CO–CH=CH_2.

   C. N≡C–CH=CH_2. D. MeO–CH=CH_2.

   (a) A. (b) B.

   (c) C. (d) D.

3. Mild warming of 3-methylcyclobutene lead to formation of ———.

   (a) 1-propene. (b) 3-*cis*-pcnta-1, 3-diene.

   (c) 3-trans ?-penta-1, 3-diene. (d) Cyclopentane.

4. Acrylonitrile can be expected to undergo cycloaddition most easily with ———.

   A. E, E-hexa-2, 4-diene. B. 2-methyl-1, 3-butadiene.

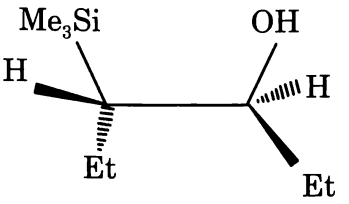
   C. Cyclohexa-1, 3-diene. D. Cyclohexa-1, 4-diene.

   (a) A. (b) B.

   (c) C. (d) D.

Turn over

5. The β-hydroxysilane shown below gives ——— with acid treatment and ——— with base treatment.



(a) Z–EtCH=CHEt ; E–EtCH=CHEt.

(b) E–EtCH=CHEt ; Z-E*t*CH=CHE*t*.

(c) Mixtures of E-EtCH=CHEt and Z-EtCH=CHEt in both cases.

(d) E–EtCH=CHEt in both cases.

6. The reagent and solvent in von Braun reaction are ——— respectively.

(a) NaCN and DMF. (b) CuCN and anhy. EtOH.

(c) Cu $(CN)_2$ and nitrobenzene. (d) CuCN and DMF.

7. Example(s) of homopolymer(s) is/are ———.

(a) Teflon.

(b) Teflon and PVC.

(c) Teflon, natural rubber and PVC.

(d) PVC, Teflon natural and styrene-butadiene rubber.

8. Condensation of two different homobifunctional monomers leads to polymer of the type ———.

(a) $-(A\text{-}A\text{-}B\text{-}B)_n-$.

(b) $-(A\text{-}B\text{-}A\text{-}B)_n-$

(c) $-(A\text{-}A\text{-}A\text{-}A\text{-}B\text{-}B\text{-}B\text{-}B)n^-$.

(d) $-(A\text{-}B\text{-}A\text{-}B\text{-}B\text{-}A\text{-}B\text{-}A)n^-$.

9. Upon Neber rearrangement, Et–C(=NOH)–Me gives ———.

(a) MeCH(–NH_2)–CH_2–Me. (b) MeCH(–NH_2)–CO–Me.

(c) MeCH(–NHCO–Me)–Me. (d) MeCH(–NHOH)–CO–Me.

10. 1 – Bromo – 4-nitrobenzene upon von Richter rearrangement affords ————.

(a) *m*-bromobenzonitrile. (b) *o*-bromobenzoic acid.

(c) *m*-bromobenzoic acid. (d) *p*-bromobenzoic acid.

11. Benzofuran can be obtained by reacting 2–OHC–C_6H_4–O–CH_2–COOH with ————.

(a) Ac_2O/AcOH ; NaOAc. (b) NaOAc in AcOH.

(c) NaOMe in EtOH. (d) gl. HOAc.

12. 6-Aminopurine is better known as ————.

(a) Adenine. (b) Guanine.

(c) Caffeine. (d) Uracil.

(12 × 1 = 12 marks)

Section B

Answer **all** *questions.*

Each question carries 2 *marks.*

13. The end products obtained in a Prins reaction depends on the reaction conditions. What products do you expect from propene and HCHO and under what conditions ?

14. Comment on the permissibility of thermal supra-supra [2 + 2] cycloaddition by applying Woodward-Hoffmann rules using Frontier Orbital method.

15. Identify the product(s) expected from the reaction of Et–SO_2–CHI–Me under condition ; (i) –Hot aq. KOH and condition ; and (ii) – K *tert*-butoxide in dry *tert*-butanol.

16. Explain the term polydispersity index of a polymer.

17. What would happen if $(C_6H_5)_3$ C–NHOH is reacted with PCl_5 ? Explain mechanistically.

18. Simple 1, 4-thiazine can exist as tautomers. Write their structures.

(6 × 2 = 12 marks)

Section C

Answer any **six** *questions.*

Each question carries 6 *marks.*

19. Robinson ring annulation involves two consecutive reactions. Explain these mechanistically.

20. Discuss the use of enamine method in α-alkylation of symmetrical and unsymmetrical ketones.

Turn over

21. Deduce the W-H selection rules pertaining to electrocyclic cyclobutene ring opening using correlation diagram method.

22. Illustrate the reaction steps and stereochemical control of olefination reactions leading to alkene synthesis.

23. Write the mechanism and uses of Mitsonobu reaction and Sommelet reactions.

24. Write a note on the stereochemical configuration of polymers.

25. Comment on the migratory aptitude of groups in rearrangement reactions. Cite examples.

26. Explain with examples Stieglitz rearrangement and Smiles rearrangement.

27. Describe the general methods for the synthesis of imidazoles and purines.

(6 × 6 = 36 marks)

Section D

Answer any **two** *questions.*

Each question carries 10 *marks.*

28. (a) Identify the HOMO and LUMO of a conjugated octatetraene and comment on their α and C2 symmetry properties.

    (b) Derive the W-H selection rules as applied to [1, 3] and [3, 3]-sigmatropic rearrangements using FMO method.

[4 + 6 = 10 marks]

29. How can the degree of polymerization and molecular weights of polymers be determined ?

30. Explain with mechanisms : Dieckmann condensation, Sharpless asymmetric epoxidation and Eschenmoser fragmentation.

[3 + 4 + 3 = 10 marks]

31. Describe the general methods for the synthesis of five membered heterocyclic compounds containing one heteroatom.

[2 × 10 = 20 marks]

C 3926 **(Pages : 4)** **Name**.....

Reg. No.....

SECOND SEMESTER P.G. DEGREE EXAMINATION, APRIL 2021

(CCSS)

Applied Chemistry

ACH 2C 06—INORGANIC CHEMISTRY—II

(2019 Admissions)

Time : Three Hours Maximum : 80 Marks

Section A

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

1. Among the following octahedral complexes which one has the highest enthalpy of hydration ?

   a) $\left[Ca(H_2O)_6\right]^{2+}$. b) $\left[Mn(H_2O)_6\right]^{2+}$.

   c) $\left[V(H_2O)_6\right]^{2+}$. d) $\left[Cr(H_2O)_6\right]^{2+}$.

2. Which electronic configuration is most likely to show spin crossover in its metal complexes ?

   a) d^3. b) d^6.
   c) d^9. d) d^8.

3. Which of the following lanthanide ion shows highest spin-only magnetic moment value ?

   a) La^{3+}. b) Sm^{3+}.
   c) Gd^{3+}. d) Tm^{3+}.

4. Which among the following will be paramagnetic ?

   a) $Cr(CO)_6$. b) $Ni(CO)_4$.

   c) $Fe(CO)_5$. d) $V(CO)_6$.

5. The rate of exchange of cyanide ligands in the complexes given follows the order ;

   (I) $\left[Ni(CN)_6\right]^{2-}$ (II) $\left[Mn(CN)_6\right]^{3-}$ (III) $\left[Cr(CN)_6\right]^{3-}$

   a) (II)>(I)>(III). b) (III)>(I)>(II).
   c) (I)<(II)<(III). d) (I)>(II)>(III).

Turn over

6. The reaction, $\left[Co(NH_3)_5 Cl\right]^{2+} + OH^- \rightarrow \left[Co(NH_3)_5 OH\right]^{2+} + Cl^-$ follows the ——— mechanistic pathway.

a) S_N1. b) S_N2.

c) $S_N1(CB)$. d) S_E2.

7. The chromium (III) species formed soon after electron transfer between $\left[IrCl_6\right]^{2-}$ and $\left[Cr(H_2O)_6\right]^{2+}$ is ———.

a) $\left[Cr(H_2O)_6\right]^{3+}$. b) $\left[Cr(H_2O)_5 Cl\right]^{2+}$.

c) $\left[Cr(Cl)_6\right]^{3-}$. d) $\left[Cr(H_2O)_3 Cl_3\right]$.

8. Oxidation of $\left[Cr(O)H_{26}\right]^{2+}$ by $\left[Co(NH_3)_5 Cl\right]^{2+}$ proceeds *via* ———.

a) Inner sphere mechanism. b) Outer sphere mechanism.

c) Complementary reactions. d) Non-complementary reactions.

9. The structure of $Fe(CO)_5$ is ———.

a) Square pyramidal. b) Trigonal bipyramidal.

c) Distorted octahedral. d) Squar plannar.

10. Among the following statements, which is wrong about Schrock carbene ?

a) Metal is in low oxidation state.

b) Non-π-accepting auxiliary ligands.

c) Carbene carbon behaves as nucleophile.

d) Non-π-donating substituents on carbon.

11. In Wilkinson's catalyst, the oxidation state and co-ordination number of the metal are respectively ———.

a) 3 and 6 b) 2 and 4.

c) 1 and 4. d) 3 and 4

12. In linear metal nitrosyls nitric oxide acts as ———.

a) One electron donor. b) Two electron donor.

c) Three electron donor. d) Five electron donor.

(12 × 1 = 12 marks)

Section B

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

13. The electronic spectra of $\left[Ti(H_2O)_6\right]^{3+}$ exhibit a broad band with a shoulder at the lower frequency region ; why ?

14. The measured magnetic moment of $K_2\left[Ni(CN)_4\right]$ and $\left[Ni(NH_3)_6\right]SO_4$ are zero and 2.83 BM respectively. Justify the observation.

15. When $\left[Pt(NO)_2Cl_3\right]^{2-}$ is treated with NH_3, which isomer of $\left[Pt(NO_2)Cl_2(NH_3)\right]^-$ is formed ? Explain.

16. Electron transfer from $\left[Fe(CN)_6\right]^{4-}$ to $\left[Fe(CN)_6\right]^{3-}$ is very fast ; why ?

17. How is methyl lithium prepared ? Discuss the structure of methyl lithium.

18. What is the role of a co-catalyst in Wacker process ?

(6 × 2 = 12 marks)

Section C

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

19. What are the distinguishing features of charge transfer bands and d-d bands ?

20. How do Orgel diagrams differ from Tanabe-Sugano diagrams ?

21. Discuss the principle involved in Gouy method for measuring the magnetic moment value of a metal complex.

22. Explain with suitable examples the different ferro and antiferromagnetic exchange pathways.

23. What are the changes that occur to a ligand when it gets co-ordinated to a metal ion ?

24. Explain how Marcus theory connects the thermodynamics and kinetics for outer sphere reactions.

25. Give an account of the classification of organometallic compounds, giving examples.

26. How is Zeise's salt synthesized ? Discuss the structure and bonding in this compound.

27. Write a note on fluxional organometallic compounds.

(6 × 6 = 36 marks)

Section D

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

28. What are the postulates of molecular orbital theory of metal complexes ? Draw the molecular orbital diagram for $\left[Ni(NH_3)_6\right]^{3+}$ species and discuss its salient features. What is the effect of π-bonding on ligand field splitting energy ?

29. a) Explain the reasons for the deviation of magnetic moment values from the spin-only values of 3d metal complexes.

    b) Write a note on the magnetic properties of *f*-block elements.

(6 + 4 = 10 marks)

30. Discuss the synthesis, structure, bonding and reactions of ferrocene.

31. Describe the mechanisms involved in oxidative addition, reductive elimination and insertion reactions of organometallic compounds giving examples.

[2 × 10 = 20 marks]

C 3925 (Pages : 4) Name.....

Reg. No.....

SECOND SEMESTER P.G. DEGREE EXAMINATION, APRIL 2021

(CCSS)

Applied Chemistry

ACH 2C 05—GROUP THEORY AND CHEMICAL BONDING

(2019 Admissions)

Time : Three Hours Maximum : 80 Marks

Section A

Choose the correct answer.

1. Which of the following does not have inversion centre ?

   (a) Td. (b) Oh.

   (c) D_4h. (d) D_3d.

2. Which of the following is *incorrect* ?

   (a) $c_{2(x)} \times c_{2y} = c_{2x}$. (b) $\sigma_{xz} \times \sigma_{yz} = c_2 z$.

   (c) $S_2 = i$. (d) ${}^3S_3 = E$.

3. The order of a group is :

   (a) Total number of symmetry operations possible on the molecule.

   (b) Total number of symmetry elements of the molecule.

   (c) The number of classes of the operation.

   (d) The highest order proper rotation axis.

4. Which of the following statements is *not* true for Alg ?

   (a) It has inversion center.

   (b) The character under C_n (principal axis) is + 1.

   (c) It is symmetric with respect to σ_h.

   (d) It is an one dimensional representation.

5. In the gamma cart the character of the matrix representing of E for cis butadiene (c_2v) is :

   (a) 1. (b) 3.

   (c) 9. (d) 30.

6. Mutual exclusion principle is not applicable to :

(a) Acetylene. (b) Ethylene.

(c) Benzene. (d) Methane.

7. The bond order of C_2 is :

(a) 1. (b) 2.

(c) 3. (d) 4.

8. The spectroscopic term symbol for ground state of O_2 is :

(a) $^3\sum_g^-$. (b) $^3\sum_g^+$.

(c) $^3\pi_g$. (d) $^3\pi_u$.

9. The delocalization energy of allyl systems follows the order :

(a) allyl cation > allyl radical > allyl anion.

(b) allyl cation < allyl radical < allyl anion.

(c) allyl radical > allyl cation > allyl anion.

(d) allyl cation = allyl radical = allyl anion.

10. London forces are :

(a) Dispersion forces. (b) Ion induced dipole.

(c) Dipole-dipole. (d) All the above.

11. An intense absorption will have the value of transition movement integral :

(a) Zero. (b) Non-zero.

(c) High non-zero. (d) Always positive.

12. Projection operator $\hat{P}_{A_1}$ for c_2v is :

(a) $1E + 1c_{2_z} + 1\sigma_{vxz} + 1\sigma_v^{'}yz.$ (b) $1E + 1c_{2_z} - 1\sigma_{vxz} - 1\sigma_v^{'}yz.$

(c) $1E - 1c_{2_z} + 1\sigma_{vxz} - 1\sigma_v^{'}yz.$ (d) $1E - 1c_{2_z} - 1\sigma_{vxz} + 1\sigma_\sigma^{'}yz.$

(12 × 1 = 12 marks)

Section B

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

13. Assign Schoonflies symbol of point groups for (a) dichloro methane ; (b) allene.
14. Reduce the representation T :

c_2v	E	c_{2_z}	σ_{vxz}	$\sigma_v^{'}yz$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	–1	–1	R_z	xy
B_1	1	–1	1	–1	x, Ry	xz
B_2	1	–1	–1	1	y', Rx	yz
T	30	0	0	10		

15. Device Gamma cart for H_2O (C_2v).
16. Write trial function for H_2 using MO theory. Justify your answer.
17. What is Frost Huckel circle mnemonic device ?
18. Distinguish between SALC and SAGO.

(6 × 2 = 12 marks)

Section C

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

19. Using Great Orthogonality theorem derive C_{4v} character table.
20. Explain block diagonalization. Illustrate its significance in simplifying quantum mechanical problems.
21. Derive reduction formula using GOT.
22. Find IR and Raman active vibrations of NH3 (C_{3v}).
23. Discuss bonding in H_2O using MO theory.
24. Apply HMO method to find the energy of pi (π) molecular orbitals of cis butadiene.

25. Predict allowed electronic transitions in Carbonyl group. Use C_{2v} character table in question No. 14.

26. Find molecular orbitals of H_2O (C_{2v}).

27. Write equation for Lennard Jones potential represent graphically. Discuss.

(6 × 6 = 36 marks)

Section D

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

28. Find hybridized orbitals of C in CH_4 (Td).

29. Compare VB and MO theory of bonding as applied to H_2. Which is better ? Justify your answer.

30. Find molecular orbitals of H_2O (C_{2v}). Predict allowed electronic transitions.

31. Discuss briefly :

    (a) Correlation diagram.

    (b) Non crossing rule.

    (c) Mutual exclusion principle.

(2 × 10 = 20 marks)

c_3v	E	$2c_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	(x, y)	$(x^2-y^2, xy)(xz, yz)$
				(R_x, R_y)	

T_d	E	$8c_3$	$3c_2$	$6s_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		$(2z^2-x^2-y^2)$
E	2	−1	2	0	0		
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, xz)