C 4715 (Pages : 2) Name.....

Reg. No.....

SECOND SEMESTER M.Sc. DEGREE (REGULAR/SUPPLEMENTARY) EXAMINATION, APRIL 2021

(CBCSS)

Chemistry

CHE 2C 08—ELECTRO CHEMISTRY, SOLID STATE CHEMISTRY AND STATISTICAL THERMODYNAMICS

(2019 Admissions)

Time : Three Hours Maximum : 30 Weightage

General Instructions

1. *In cases where choices are provided, students can attend* **all** *questions in each section.*
2. *The minimum number of questions to be attended from the Section / Part shall remain the same.*
3. *There will be an overall ceiling for each Section / Part that is equivalent to the maximum weightage of the Section / Part.*

Section A

Answer any **eight** *questions.*
Each question carries a weightage of 1.

1. Write electrode reactions for $H_2 - O_2$ fuel cell under alkaline conditions.
2. Find electrode potential for a calomel electrode with 0.1 M kCl. The standard electrode potential is 0.268 V, T = 298 K.
3. What is Stern model of electrical double layer ?
4. What is half wave potential ? Explain its significance.
5. Write Schoenflies symbol for (a) 222 ; (b) mmm.
6. Account for the semiconductivity of nonstoichiometric ZnO.
7. Explain ferrimagnetism. Write one example.
8. Explain thermodynamic probability. How is it related to entropy ?
9. Find symmetry number for (a) C_6H_6 ; (b) CH_4.
10. Calculate the heat capacity for diamond at 1.86 K characteristic temperature is 1860 K.

(8 × 1 = 8 weightage)

Section B

Answer any **six** *questions.*
Each question carries a weightage of 2.

11. Calculate the concentration of Ag^+ at equilibrium, when excess of finely divided metallic Ag is added to 0.05 molal ferric nitrate. The standard electrode potentials of Ag^+/Ag and Fe^{2+}, Fe^{3+} | Pt are 0.799 and 0.771 V respectively. T = 298 K.
12. Calculate the thickness of ion atmosphere around k^+ in 0.01 KCl at 25°C in water. The dielectric constant = 78.5.
13. Discuss one of the theories of hydrogen over voltage.
14. List the seven crystal systems and corresponding Bravais lattices. Discuss.
15. What is Piezoelectricity ? Discuss its applications.
16. Define partition function. Derive equation to show its relationship with internal energy.
17. Calculate absolute entry of He at 0°C and 1 atmosphere pressure.
18. Show that all particles obey Maxwell-Boltzman statistics under dilute system conditions.

(6 × 2 = 12 weightage)

Section C

Answer any **two** *questions.*
Each question carries a weightage of 5.

19. What are the assumptions of Debye Huckel theory ? Using the theory derive Debye Huckel limiting law.
20. Derive Butler-Volmer equation.
21. Briefly discuss free electron theory of metals.
22. Discuss Debye's theory of heat capacity of solids.

(2 × 5 = 10 weightage)

SECOND SEMESTER M.Sc. DEGREE (REGULAR/SUPPLEMENTARY) EXAMINATION, APRIL 2021

(CBCSS)

Chemistry

CHE 2C 07—REACTION MECHANISM IN ORGANIC CHEMISTRY

(2019 Admissions)

Time : Three Hours Maximum : 30 Weightage

General Instructions

1. *In cases where choices are provided, students can attend* **all** *questions in each section.*
2. *The minimum number of questions to be attended from the Section / Part shall remain the same.*
3. *There will be an overall ceiling for each Section / Part that is equivalent to the maximum weightage of the Section / Part.*

Section A

Answer any **eight** *questions.*
Each question carries a weightage of 1.

1. What are ambident nucleophiles ? Explain with examples.
2. In aromatic electrophilic substitution reactions, each hydrogen atom of donor-substituted aromatic compound should be substituted faster than a H atom in benzene and each hydrogen atom of acceptor-substituted aromatic compound should be substituted more slowly than a H atom in benzene. Explain.
3. Explain the mechanism of Hofmann elimination, highlighting the stereochemical relationship of the substrate and product.
4. Arrange the following in order of stability : CF_2, : CCl_2, : CBr_2 and CH_2. Justify.
5. Indicate the mechanism of Dieckmann condensation reaction. Comment on the synthetic utility of this reaction.
6. Predict the product in the CN^- catalyzed condensation of benzaldehyde and p-dimethylaminobenzaldehyde. Indicate mechanism involved.
7. Given the triplet energies of norbornene (70 - 78), benzophenone (70) and acetophenone (78), predict the products obtained when each of the ketone is irradiated with norbornene.

8. Write down the mechanism of di-pi methane rearrangement.

9. Illustrate Paterno-Büchi reaction with a suitable example.

10. Cholesterol undergoes oxidation of side chain under various conditions. Give the structure of two major products formed in these reactions.

(8 × 1 = 8 weightage)

Section B

Answer any **six** *questions.*
Each question carries a weightage of 2.

11. Explain the SNAr and SRN1 mechanisms of aromatic nucleophilic substitution with a suitable examples.

12. Explain the ion-pair mechanism of nucleophilic aliphatic substitution. Comment on the stereochemical outcome in such reactions.

13. Substitution and elimination reactions are often competing reactions. Why ? What are the precautions to be taken to get the desired products ?

14. Briefly discuss the main pathways of generation of carbanions. Comment on their structure and stability.

15. Explain Mannich reaction with an appropriate example.

16. Predict whether the thermal ring closure of a compound with three conjugated pi-bonds is conrotatory or disrotatory. Explain.

17. Explain the following terms : i) photosensitization ; ii) quenching ; and iii) photoenolization.

18. Write a brief note on general structure and properties of anthocyanins.

(6 × 2 = 12 weightage)

Section C

Answer any **two** *questions.*
Each question carries a weightage of 5.

19. Discuss the mechanisms of electrophilic aromatic substitution with special reference to substituent effect on reactivity and orientation in mono and disubstituted benzene rings.

20. Discuss the major acid and base catalyzed mechanisms of ester hydrolysis.

21. Give one example each of : i) thermally allowed cycloaddition reaction ; and ii) photochemically allowed electrocyclic reaction. Justify the answer by FMO method.

22. Discuss the salient features of total synthesis of longifolene.

(2 × 5 = 10 weightage)

SECOND SEMESTER M.Sc. DEGREE (REGULAR/SUPPLEMENTARY) EXAMINATION, APRIL 2021

(CBCSS)

Chemistry

CHE 2C 06—CO-ORDINATION CHEMISTRY

(2019 Admissions)

Time : Three Hours Maximum : 30 Weightage

General Instructions

1. *In cases where choices are provided, students can attend* **all** *questions in each section.*
2. *The minimum number of questions to be attended from the Section / Part shall remain the same.*
3. *There will be an overall ceiling for each Section / Part that is equivalent to the maximum weightage of the Section / Part.*

Section A

Answer any **eight** *questions.*

Each question carries a weight of 1.

1. Which is stabler ; EDTA complex of Mg^{2+} or Ca^{2+} ? Substantiate your answer.
2. The successive formation constants for the formation of $[CdBr_4]^{2-}$ in aqueous medium are : $K_1 = 36.2$, $K_2 = 3.47$, $K_3 = 1.15$, $K_4 = 2.34$. Explain why $K_4 > K_3$?
3. The nephelauxetic effect produced by CN-is greater than that of NH_3 ; why ?
4. Why tetrahedral complexes are always of high-spin ?
5. Differentiate between microstate and atomic state.
6. Arrive at the ground state term symbols for metal ions with the following electronic configuration :

   (a) $3d^5 4s^0$; (b) $3d^8 4s^0$.

7. How infrared spectroscopy can be used to identify intermolecular and intramolecular hydrogen bonding in ligand systems ? Explain.

8. What information do you gather from chemical shift observed in NMR spectra of ligands and metal complexes ? Explain with suitable examples.

9. Explain aquation reaction in metal complexes with a suitable example.

10. Explain the mechanism and catalysts involved in photolysis of water in photosynthetic process.

(8 × 1 = 8 weightage)

Section B

Answer any **six** *questions.*
Each question carries a weight of 2.

11. Discuss the factors that affect the stability of metal complexes.

12. What is Jahn-Teller distortion ? Which of the following are expected to show this type of distortion ? Explain :

    (a) $[Cr(acac)_3]$. (b) $[Co(CN)_6]^{4-}$.

    (c) $[CuCl_6]^{4-}$.

13. Octahedral cobalt (II) complexes have higher magnetic moment values than tetrahedral cobalt (II) complexes ; why ?

14. An iron (II) complex exhibits a Mössbauer peak at 98 K, while at 155 K it gives two peaks. What might be the reason for this temperature dependent behavior ?

15. Explain the factors that affect the rate of substitution reaction in metal complexes.

16. Write a note on metal complex sensitizers.

17. Sketch the different bonding modes of acetate group towards a metal ion. How infrared spectroscopy can be used to identify these bonding modes ?

18. Differentiate between chelate effect and macrocyclic effect with suitable examples. Compare the stabilities of $[Cu(en)_2(H_2O)_2]^{2+}$ and $[Cu(en)_3]^{2+}$ (en = ethylenediamine).

(6 × 2 = 12 weightage)

Section C

Answer any **two** *questions.*

Each question carries a weight of 5.

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

20. (a) Give an account of the ferromagnetism and antiferromagnetism exhibited by metal complexes.

    (b) Describe the experimental details for finding out the magnetic moment value of a solid metal complex. What is the significance of Pascal's constants in this experiment ?

(2 + 3 = 5 weightage)

21. What is trans effect ? What are the important theories put forward to explain it ? Explain any *one* of its synthetic applications.

22. Discuss the mechanisms involved in outer-sphere and inner-sphere electron transfer reactions of metal complexes, bringing out the factors favouring these reactions.

[2 × 5 = 10 weightage]

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SECOND SEMESTER M.Sc. DEGREE (REGULAR/SUPPLEMENTARY) EXAMINATION, APRIL 2021

(CBCSS)

Chemistry

CHE 2C 05—GROUP THEORY AND CHEMICAL BONDING

(2019 Admissions)

Time : Three Hours Maximum : 30 Weightage

General Instructions

1. *In cases where choices are provided, students can attend* **all** *questions in each section.*
2. *The minimum number of questions to be attended from the Section / Part shall remain the same.*
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Section A

Answer any **eight** *questions.*
Each question carries a weightage of 1.

1. Assign Schoenflies symbol of point group :
   (a) Allene. (b) Dichloromethane.
2. Find the similarity transform of any one of the vertical planes in NH_3.
3. Generate matrices using positional co-ordinates x, y, z :
   (a) S_4. (b) C_3.
4. Distinguish between degenerate and non-degenerate representations with examples.
5. Explain with one example non-vanishing integral.
6. Cis butadiene belongs c_{2v} point group. Find the character under E in the gamma cart.
7. Write projection operator $\hat{P}_{Ag}$ for c_{2h}. The operations are E, c_{2z}, $\sigma_h x_y$ and i.
8. State and explain Born–Oppenheimer approximation.
9. Write spectroscopic term symbol of :
   (a) O_2. (b) N_2.
10. State and explain Laporte selection rules.

(8 × 1 = 8 weightage)

Turn over

Section B

Answer any **six** *questions.*
Each question carries a weightage of 2.

11. Explain the importance of block diagonalization in solving quantum mechanical problem using group theory.
12. Derive C_3 character table.
13. Find IR and Raman active vibrations of H_2O (c_{2v}).
14. Find molecular orbitals of HCHO. Use c_{2v} character table.
15. Find bond energy of π – molecular orbitals of benzene by HMO method.
16. Discuss Frost Hückel mnemonic device for cyclic polymers.
17. Show that the four symmetry operations E, c_{2z}, $\sigma_h x_y$ and i form a mathematical group under multiplication.
18. List the symmetry operations possible on D_{4h}. Classify them into different classes of operations.

(6 × 2 = 12 weightage)

Section C

Answer any **two** *questions.*
Each question carries a weightage of 5.

19. Find hybridized orbitals of C in CH_4. Use Td character table.
20. Find $\pi(pi)$ molecular orbitals of *cis butadiene* by HMO method. Use c_{2v} character table.
21. Discuss V.B. method of bonding as applied to H_2.
22. (a) Setup group multiplication tables for c_{3v}.
    (b) State and explain rules for assigning Mulliken's symbol for symmetry species.

c_{2v}	E	c_{2z}	$\sigma_v x_z$	$\sigma' vyz$		
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	xyz

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		
E	2	–1	2	0	0		$(2z^2 - x^2 - y^2)$
T_1	3	0	–1	1	–1	(Rx, Ry,Rz)	
T_2	3	0	–1	–1	1	(x, y, z)	(xy, xz, yz)

(2 × 5 = 10 weightage)

SECOND SEMESTER M.Sc. DEGREE (SUPPLEMENTARY) EXAMINATION APRIL 2021

(CUCSS)

Chemistry

CH 2C 08—ELECTRO CHEMISTRY, SOLID STATE CHEMISTRY STATISTICAL THERMODYNAMICS

(2015 Admissions)

Time : Three Hours Maximum : 36 Weightage

Section A

Answer **all** *questions.*
Each question carries a weightage of 1.

1. Define mean ionic activity coefficient.
2. Write electrode reaction for calomel electrode. What is the corresponding Nernst equation ?
3. What is Stern model of electrical double layer ?
4. Define concentration over potential.
5. Write Schoenflies symbol for (a) mmm ; (b) 2 mm.
6. Write one example for crystal showing both Schottky and Frenkel defect.
7. Define Fermi level. Explain its significance.
8. Explain with example color center.
9. Rationalise third law of thermodynamics using statistical concepts.
10. Show that molecular partition function is the product of the partition function for the various degrees of freedom.
11. Electrons never follow Maxwell Boltzman statistics. Why ?
12. Calculate heat capacity of a solid at 2.12 K. Its characteristic temperature is 212 K.

(12 × 1 = 12 weightage)

Section B

Answer any **eight** *questions.*
Each question carries a weightage of 2.

13. Discuss the working of a lead acid battery.
14. The EMF of the cell $Pt\left|{}^{H_2}_{1b}\right\|{}^{HBr}_{0.1m}\left|{}^{AgBr}_{(s)}\right|Ag$ is 0.3524 V at 25°C. Find the activity coefficient of 0.1 m HBr. The standard electrode potential of $Br^- | AgBr_{(s)} | Ag$ is 0.2224 V.

15. Discuss one of the theories of hydrogen over voltage.
16. What are the advantages of dropping mercury electrode in Polarography ?
17. Draw stereographic projection for monoclinic system. Discuss.
18. Write a brief account of non-stoichiometric compounds.
19. Discuss briefly Cooper theory of superconductivity.
20. Define Piezoelectricity. Discuss its applications.
21. Calculate the ratio of population at 300 K for energy levels separated by 1000 cm^{-1}. The ground state is non-degenerate and excited state is triply degenerate.
22. Derive equation to show the relationship between partition function and (a) internal energy ; and (b) entropy.
23. Show that all particles follow Maxwell Boltzman Statistics under dilute system conditions.
24. Derive Fermi Dirac distribution law.

(8 × 2 = 16 weightage)

Section C

Answer any **two** *questions.*
Each question carries a weightage of 4.

25. Briefly discuss band theory of solids.
26. Discuss briefly Debye's theory of heat capacity of solids.
27. What is Bose-Einstein condensation ? Discuss.
28. Write a brief account of magnetic properties of solids.

(2 × 4 = 8 weightage)

C 4553 **(Pages : 2)** **Name.....**

Reg. No.....

SECOND SEMESTER M.Sc. DEGREE (SUPPLEMENTARY) EXAMINATION APRIL 2021

(CUCSS)

Chemistry

CH 2C 07—REACTION MECHANISM IN ORGANIC CHEMISTRY

(2015 Admissions)

Time : Three Hours Maximum : 36 Weightage

Section A

Answer **all** *questions.*

Each question carries a weightage of 1.

1. What are the effects of substrate structure on the reactivity of S_N1 reaction ?
2. What is the best solvent for organic reaction ? Why ?
3. What is Saytzev rule ?
4. Write two methods for the generation of carbenes.
5. What is Thorpe condensation ?
6. Why Zinc is the best catalyst for Reformatsky reaction.
7. What are 'ene' reactions ? Give two examples.
8. What are group transfer reactions ? Give an example.
9. What is mean by spin multiplicity ?
10. What is photoisomerization of alkene ?
11. What are steroids ?
12. Discuss the structure of atropine.

(12 × 1 = 12 weightage)

Section B

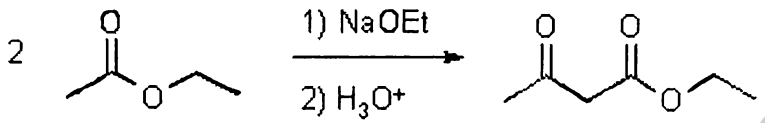
Answer **all** *questions.*

Each question carries a weightage of 2.

13. Discuss the mechanism and stereochemical aspects of S_{N2} reaction.
14. Explain the SET mechanism.

Turn over

15. Distinguish between ElcB and El mechanisms.
16. Discuss the mechanism of Michael reaction.
17. Briefly explain the effect of substituents on the rate and orientation of addition reactions.
18. Discuss the stability and reactions of carbocations.
19. Discuss the mechanism of Perkin reaction.
20. Write down the mechanism of :



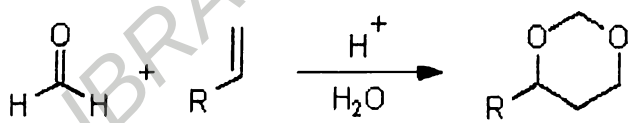
21. Explain with suitable example the Norish type-II cleavage.
22. Discuss the mechanism of Photo Fries rearrangement.
23. Explain the classifications of Terpenoids.
24. How will you convert cholesterol to testosterone ?

(8 × 2 = 16 weightage)

Section C

Answer **two** *questions.*
Each question carries a weightage of 4.

25. Explain the mechanism and stereochemistry of S_E2 (front and back) reaction.
26. (a) What are extrusion reactions? Give examples.
    (b) Discuss the mechanism of :



27. (a) What is Jablonski diagram ?
    (b) What is Paterno-Buchi reaction ? Discuss its mechanism. What are its applications ?
28. Explain the total synthesis of Reserpine.

(2 × 4 = 8 weightage)

C 4551 **(Pages : 3)** **Name.....**

Reg. No.....

SECOND SEMESTER M.Sc. DEGREE (SUPPLEMENTARY) EXAMINATION APRIL 2021

(CUCSS)

Chemistry

CH 2C 05—APPLICATIONS OF QUANTUM MECHANICS AND GROUP THEORY

(2015 Admissions)

Time : Three Hours Maximum : 36 Weightage

Part A

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

1. Why approximations are needed to solve the Schrödinger equation of many electron systems ?
2. Write down the Schrodinger equation for a n - electron system under independent particle model and comment on its solutions.
3. What are the allowed spin functions for an electron ?
4. Write down determinantal wave function for the electronic configuration $1s^2\ 2s^1$ and demonstrate Pauli's exclusion principle.
5. Write down the Schrodinger equation for H_2 molecule and explain each term.
6. State Born-Oppenheimer approximation. Explain the Hamiltonian operator terms neglected in Born-Oppenheimer approximation.
7. Using Frost diagrams, predict the aromatic/antiaromatic/non aromatic nature of i) cyclopropenyl cation ; ii) cyclopentadienyl anion ; iii) cyclobutadiene ; iv) cyclooctatetraenyl dianion.
8. What is free valence index ? What does this indicate ?
9. What are vanishing and non-vanishing integrals ?
10. Write down the selection rules for electronic transitions.
11. What are projection operators ?
12. Define coulomb and exchange integrals.

(12 × 1 = 12 weightage)

Turn over

Part B

Answer any **eight** *questions.*
Each question carries 2 *weightage.*

13. State and prove variational theorem.
14. Calculate the first order perturbation correction to ground state energy of Helium atom.
15. What are spin orbitals ? What is the spin orbital of an atom of electronic configuration $1s^2$?
16. Illustrate non-crossing rule with an example.
17. Draw the molecular orbital diagram of O_2. Derive the term symbols for O_2 and arrange them in the order of their energies.
18. Write down the limitations of Hartree-Fock theory.
19. Differentiate STO and GTO.
20. Compare and contrast MO and VB theories.
21. Calculate the variation energy for the following trial function for the hydrogen atom, $\phi = e^{-(\alpha r^2)}$.
22. Construct the symmetry adapted linear combinations for the π -orbitals of cyclopropenyl cation.
23. HCHO belongs to C2v point group. Find the allowed electronic transitions of the molecule.
24. Outline the steps involved in Hartree Fock self consistent field theory of atoms.

(8 × 2 = 16 weightage)

Part C

Answer any **two** *questions.*
Each question carries 4 *weightage.*

25. Derive the permitted energies of the π -electron system in butadiene by HMO method and show the ground state electronic configuration of this molecule. Also derive the molecular orbitals.
26. Outline the solution of the Schrodinger equation for H_2 molecule within the molecular orbital theory approximation.
27. Explain how group theory enables one to construct the hybrid orbitals of molecules taking H_2O as an example (C_{2v}).

28. Find out the total molecular vibrations of NH_3 molecule using (C_{3v}) character table. Identify the IR and Raman activity of these vibrations.

C_{2v}	E	C_{2z}	σ_{vxz}	$\sigma_{v'yz}$
A_1	1	1	1	1
A_2	1	1	–1	–1
B_1	1	–1	1	–1
B_2	1	–1	–1	1

C_{3v}	E	$2C_3$	$3\sigma v$
A_1	1	1	1
A_2	1	1	–1
E	2	–1	0

(2 × 4 = 8 weightage)