

**FIRST SEMESTER M.Sc. DEGREE (REGULAR/SUPPLEMENTARY)
EXAMINATION, NOVEMBER 2020**

(CBCSS)

Chemistry

CHE 1C 04—THERMODYNAMICS, KINETICS AND CATALYSIS

(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. Explain with examples 'residual entropy'.
2. Define 'excess thermodynamic functions'. Explain its significance.
3. Explain terms 'forces and fluxes' with reference to irreversible process.
4. State and explain Glansdorf Pregogine theorem.
5. State and explain steady state approximation.
6. Explain pressure jump method of relaxation spectroscopy.
7. Distinguish between Diffusion Controlled and Activation Controlled reactions.
8. Distinguish between Collision Cross Section and Reaction Cross Section.
9. Define isosteric heat of adsorption. Explain its significance.
10. Unimolecular gas phase reactions follow first order kinetics at low pressures and zero order kinetics at high pressures. Why ?

(8 × 1 = 8 weightage)

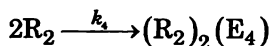
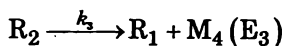
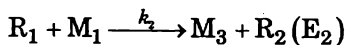
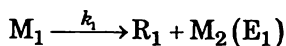
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Section B

Answer any **six** questions.

Each question carries a weightage of 2.

11. Define Fugacity. How is it determined ? Discuss.
12. Write Duhern Margules equation. Use the equation to show that solvent obeys Rault's law in the limit of solute obeying Henry's law.
13. Define phenomenological co-efficient. Show that direct co-efficient always dominate indirect co-efficients.
14. An organic decomposition reaction follow the mechanism.



Assuming steady state approximation for R_1 and R_2 derive the rate law. E_1, E_2, E_3, E_4 are the activation energies for the elementary steps. Find the apparent activation energy.

15. Derive an equation to show the effect of dielectric constant of the medium on the rate of ionic reaction in solution.
16. Briefly discuss a crossed molecular beam experiment.
17. How would you determine surface acidity of the solid using TPD of ammonia ? Discuss.
18. Discuss Lotka Volterra model of oscillating chemical reactions.

(6 × 2 = 12 weightage)

Section C

Answer any **two** questions.

Each question carries a weightage of 5.

19. Rationalise :
(a) Thermal Osmosis. (b) Thermal Diffusion using irreversible thermodynamic.
20. What are the methods of studying fast reaction ? Discuss.
21. Discuss briefly. 'Activated Complex theory' of reaction rates.
22. What are the methods for the determination of surface area of solids ? Discuss.

(2 × 5 = 10 marks)

**FIRST SEMESTER M.Sc. DEGREE (REGULAR/SUPPLEMENTARY)
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(CBCSS)

Chemistry

CHE 1C 03—STRUCTURE AND REACTIVITY OF ORGANIC COMPOUNDS

(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.*
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Section A

Answer any eight questions.

Each question carries a weight of 1.

1. Cyclopentadiene has a pka value 15 which is quite high (for a H bonded to sp³ carbon). Account for this observation.
2. Instead of adopting a planar structure assisting complete overlap of its p orbitals, cyclooctatetraene exists as a tub shaped molecule. Explain.
3. Differentiate between classical and non-classical carbocations.
4. What are conformationally biased molecules? Give examples.
5. Draw the preferred conformation of *trans*- and *cis*-1-methyl-3-isopropylcyclohexane.
6. What are the destabilizing interactions present in axially substituted cyclohexanes ?
7. Write down the structure of a prochiral compound and assign the stereodescriptor for the prochiral center.
8. Draw all 1, 3-dimethyl cyclohexanes. Which of these are chiral ?
9. What are chiral auxiliaries ? Give an example of one used in asymmetric Diels-Alder reactions.
10. Illustrate Sharpless asymmetric epoxidation reaction and specify the reagents and conditions employed.

(8 × 1 = 8 weightage)

Turn over

Section B

Answer any six questions.

Each question carries a weight of 2.

11. Discuss the effect of resonance on the acidity of carboxylic acids. Give examples.
12. Explain the aromaticity of cyclopentadienyl anion and [18] annulene, based on Huckel's rule.
13. State Hammond postulate and apply it to predict the relative rates of solvolysis of 2-bromopropane and 2-methyl-2-bromopropane.
14. Illustrate the terms kinetic and thermodynamic control with appropriate examples.
15. Explain the origin of optical isomerism in certain cummulenes and biphenyls.
16. What is the basic principle involved in resolution of racemates ? Explain the application of S-brucine in resolution ?
17. Explain the stereochemistry of reduction with CBS reagent with any suitable example.
18. With a suitable example, explain an asymmetric aldol reaction by Zimmerman-Traxler model.

(6 × 2 = 12 weightage)

Section C

Answer any two questions.

Each question carries a weight of 5.

19. Discuss the effect of hydrogen bonding on the physical and chemical properties (including reactivity) of organic compounds. How does hydrogen bonding affect conformation of 1, 2-, 1, 3- and 1, 4-cyclohexanediols ?
20. (a) Write a detailed note on the application of isotope effects in the study of reactions mechanisms. Discuss with suitable examples.
(b) Write a brief note on Bredt's rule.
21. Discuss the effect of conformation on the course and rate of reactions in cyclohexane systems citing sufficient example.
22. (a) Explain the concept of asymmetric induction and illustrate the prediction of stereochemical outcome with Felkin-Ahn model, in an appropriate example.
(b) Write a note on symmetric hydroboration reactions.

(2 × 5 = 10 weightage)

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Chemistry

CHE 1C 02—ELEMENTARY INORGANIC CHEMISTRY

(2019 Admissions)

Time : Three Hours

Maximum : 30 Weightage

General Instructions

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Section A

Answer any eight questions.

Each question carries a weightage of 1.

1. The electrical conductivity of liquid ammonia is increased when ammonium chloride is dissolved in it ; why ?
2. What is symbiosis ? Explain.
3. Classify the following into *closo* / *nido* / *arachno* structures :
a) B_5H_9 b) $(B_8H_8)^{2-}$ c) $C_2B_3H_5$ d) B_4H_{10}
4. Discuss the consequences of isomorphous substitution in silicates.
5. Explain, why $P_4N_4Cl_8$ is puckered while $P_4N_4F_8$ is planar ?
6. What are interstitial carbides ? Give examples.
7. What are Ellingham diagrams ? Account for the abrupt changes in these diagrams.
8. What is the significance of 'Q' values in nuclear reactions ?
9. How is uranyl sulphate prepared ? Give the equation.
10. Comment on the size-dependent properties of cadmium selenide.

(8 × 1 = 8 weightage)

Turn over

Section B

Answer any six questions.

Each question carries a weightage of 2.

11. Explain Lux-Flood theory of acids and bases.
12. What are Frost diagrams ? Discuss their applications.
13. How do substituted borazines are prepared ? Give a brief account of the structure and bonding in borazine.
14. Give a brief account of the synthesis, structure and properties of $(\text{SN})_x$, S_2N_2 and S_4N_4 .
15. Discuss the principle involved in neutron activation analysis.
16. Write a note on trans-actinide elements.
17. How do graphenes differ from fullerenes ?
18. Write briefly on diagnostic and therapeutic applications of nanomaterials.

(6 × 2 = 12 weightage)

Section C

Answer any two questions.

Each question carries a weightage of 5.

19. Give the important characteristics of ammonia as a solvent. Discuss briefly, the precipitation reaction that occur in ammonia.
20. How is 1, 2-dicarba-closo-dodecaborane(12) prepared ? Write a note on its isomerism. Compare the acidity of the different types of hydrogen atoms present in carboranes.
21. a) Write an account on the synthesis, structure and uses of silicones.
b) Write briefly on the classification of carbides.
22. Write an account on heteropoly and isopoly anions of W and Mo.

(2 × 5 = 10 weightage)

**FIRST SEMESTER M.Sc. DEGREE (REGULAR/SUPPLEMENTARY)
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(CBCSS)

Chemistry

CHE 1C 01—QUANTUM MECHANICS AND COMPUTATIONAL CHEMISTRY

(2019 Admissions)

Time : Three Hours

Maximum : 30 Weightage

Section A

Answer any eight questions.

Each question carries a weightage of 1.

1. Write time dependent Schrödinger wave equation. Mention one application.
2. Which of the following are eigen functions of $\frac{d^2}{dx^2}$? Find the corresponding eigen values :
 - (a) $A \sin kx$.
 - (b) e^{x^2} .
 - (c) $\log x$.
 - (d) e^{-ax} .
3. A particle is confined to one dimensional box of length 'a'. What is the degeneracy associated with the level having energy $\frac{14 h^2}{8 ma^2}$.
4. Write recursion formula for a simple harmonic oscillator. Explain its significance.
5. Represent \hat{L}_z in (a) Cartesian co-ordinates ; (b) Spherical polar co-ordinates.
6. Explain with example 'spin orbital'.
7. State and explain independent particle model.
8. What is STO ? Write one example.
9. Explain the concept of force field in computational chemistry.
10. Write Z-matrix for H₂O.

(8 × 1 = 8 weightage)

Turn over

Section B

Answer any **six** questions.

Each question carries a weightage of 2.

11. Define Hermitian operator. Show that Hermitian operators always have real eigen values.
12. A particle in one-dimensional box of length a is given by the state function $\sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}\right)x$. Find the average value of momentum along x direction. Justify your answer.
13. Find eigen functions and eigen values for a planar rotor.
14. Is wave function for H atom is Ne^{-r/a_0} . Show that the maximum probability of finding the electron is at $r = a_0$.
15. State and prove variation theorem.
16. Briefly discuss Hartree Fock self consistent field method of solving many electron atoms.
17. Write a brief account of semi empirical methods of computational Chemistry.
18. Briefly discuss structure of a Gaussian input file.

(6 × 2 = 12 weightage)

Section C

Answer any **two** questions.

Each question carries a weightage of 5.

19. Briefly discuss postulates of quantum mechanics.
20. Apply Schrödinger equation for one dimensional simple harmonic oscillator. Find eigen functions and eigen values.
21. Apply Schrödinger wave equation for H atom transform into spherical polar co-ordinates. Separate the variables. Solve the $\psi(\phi)$ equation.
22. Use perturbation method to find the ground state energy for a particle in one dimensional box with slanted bottom.

(2 × 5 = 10 weightage)

**FIRST SEMESTER M.Sc. DEGREE (SUPPLEMENTARY) EXAMINATION
NOVEMBER 2020**

(CUCSS)

Chemistry

CH 1C 04—THERMODYNAMICS, KINETICS AND CATALYSIS

(2015 Admissions)

Time : Three Hours

Maximum : 36 Weightage

Section A

Answer all questions.

Each question carries a weight of 1.

1. “ Entropy of the universe is always increasing” explain.
2. Give the expression for collision frequency and explain the terms.
3. Write a short note on TEM
4. Represent London equation and explain its significance.
5. What are phenomenological Laws ?
6. Explain the term residual entropy.
7. Explain the basic assumptions of Langmuir-Hinshelwood mechanism of surface catalyzed reactions.
8. What are primary and secondary salt effects ?
9. What is acid - base catalysis explain with the help of examples ?
10. Explain the principle of flash photolysis.
11. Represent BET isotherm. Explain the condition under which BET isotherm approximates to Langmuir adsorption isotherm ?
12. What is meant by thermal diffusion ?

(12 × 1 = 12 weightage)

Turn over

Section B

Answer any **eight** questions.

Each question carries a weightage of 2.

13. What is meant by thermodynamics of mixing ?
14. Derive the rate equation for thermal decomposition of ethane.
15. Discuss Oregonator model of oscillating reactions.
16. B-Galactosidase enzyme catalyzed hydrolysis of lactose at 298K has Michealis constant of 0.065 mol L⁻¹. At a substrate concentration of 0.75 mol L⁻¹, the reaction rate is found to be 3.15 mol L⁻¹ s⁻¹. Calculate the maximum velocity.
17. Discuss briefly the different factors affecting the kinetics of reaction in solution phase.
18. Derive Langmuir adsorption isotherm.
19. A gas obeys the equation of state $P(V_m - b) = RT$. For this gas $b = 0.0391 \text{ dm}^3 \text{ mol}^{-1}$. Calculate fugacity and fugacity coefficient for the gas at 1000°C and 1000 atm.
20. What is the surface area of the solid if 118 ml of H₂ formed a monolayer on silica gel at STP ? The cross sectional area of H₂ is 0.192 nm².
21. Explain Hinshelwood modification for Lindemann's hypothesis
22. Give the rate of entropy production. Show that $\sum J_i X_i > 0$, for an irreversible system where a temperature gradient exists.
23. Explain the determination of partial molar volume of a binary mixture.
24. Write a note on electrokinetic effects.

(8 × 2 = 16 weightage)

Section C

Answer any **two** questions.

Each question carries a weightage of 4.

25. Discuss the salient features of conventional transition state theory (CTST). Derive the equation for the rate constant
26. Prove Onsager reciprocal relationship applying the principle of microscopic reversibility
27. Derive the kinetics of H₂ – O₂ reaction
28. Derive Michaelis-Menton equation and explain the pH and temperature dependence

(2 × 4 = 8 weightage)

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Chemistry

CH 1C 03—STRUCTURE AND REACTIVITY OF ORGANIC COMPOUNDS

(2015 Admissions)

Time : Three Hours

Maximum : 36 Weightage

Section A

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

1. Explain inter and intra molecular hydrogen bonding with suitable examples. How does it effect the volatility of compounds ?
2. Explain bonding in ylides.
3. Vinyl halides are less reactive than alkyl halides. Why ?
4. Explain Marcus theory of electron transfer.
5. Comment on the conformation of *cis*-1, 4-dit.butyl cyclohexane.
6. Comment on the conformation and chirality of decalin.
7. What do you mean by dihedral angle ?
8. Which is the most favourable conformation of methyl cyclohexane ? Why ?
9. Draw the stereo isomers of benzaldoxime and name them.
10. Propanoic acid undergoes HVZ reaction and gives 2- bromopropanoic acid. Sketch the optical isomers of the product.
11. Explain cyclopropanation of styrene in presence of a chiral ligand ?
12. Write down the structures of (i) DIP AMP ; and (ii) BINAP.

(12 × 1 = 12 weightage)

Turn over

Section B

Answer any **eight** questions.

Each question carries 2 weightage.

13. Represent the molecular orbitals of 1, 3-butadiene and indicate the HOMO and LUMO under thermal and Photochemical conditions.
14. Explain the terms aromaticity, antiaromaticity and homoaromaticity with suitable examples.
15. What do you mean by Hard and Soft electrophiles and nucleophiles ?
16. Explain kinetic and thermodynamic control of reactions.
17. Represent the conversion of one chair form of cyclohexane to its alternate form through different conformations.
18. What do you mean by dihedral angle ? Explain the variation of energy against dihedral angle of conformations of ethane.
19. Give the mechanism of deamination of different conformations of 2-aminocyclohexanol with nitrous acid.
20. Optically active 2-methyl-1, 2-Butandiol undergoes Wagner-Meerwein rearrangement to give a racemic mixture of products. Explain ?
21. Write the structures of all the possible monochloro pentanes. Which are enantiomers ? Specify them as R and S.
22. Write a note on 1, 3- diaxial interactions in Cyclohexane and its derivatives.
23. Explain Felkin model of asymmetric induction ?
24. Write a note on asymmetric Diels'Alder reactions.

(8 × 2 = 16 weightage)

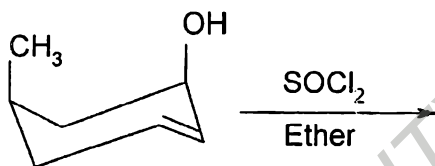
Section C

Answer any **two** questions.

Each question carries 4 weightage.

25. Explain :
 - i) Enantioselective catalytic hydrogenation developed by Noyori and Knowels.
 - ii) Asymmetric aldol condensation pioneered by Evans.
26.
 - a) What is meant by resolution ?
 - b) Explain two methods for the resolution of racemic mixture.
 - c) Briefly explain the rules for assigning E and Z configuration for geometrical isomers.

27. a) Elimination of HBr from 2-bromobutane gives both cis and trans 2-butene. Why ?
b) Explain the dehalogenation of stereoisomers of 2, 3-dibromobutanes.
28. a) When optically active threo-3-bromo-2-butanol is treated with HBr, we get a racemic mixture of threo-dibromide. Explain ?
b) When 2-bromo propanoic acid is treated with dilute alkali, a lactate ion with retention of configuration is obtained. Explain ?
c) Complete the reaction :



(2 × 4 = 8 weightage)

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CH 1C 02—ELEMENTARY INORGANIC CHEMISTRY

(2015 Admissions)

Time : Three Hours

Maximum : 36 Weightage

Section A

Answer all questions.

Each question carries 1 weightage.

1. Why H_2O is liquid and H_2S is gas at normal temperature ?
2. Describe the change in hybridisation of aluminium atom during the reaction :
$$\text{AlCl}_3 + \text{Cl}^- \rightarrow \text{AlCl}_4^-$$
3. Define Acid and Base according to Usanovich concept.
4. Write Drago-Wayland equation and explain the terms
5. Calculate the “styx” numbers of B_5H_{10} .
6. What is Graphene ?
7. What is meant by molecular sieves ?
8. List the applications of silicones.
9. What is Uranates ?
10. Write down the names of four elements which are accepted by IUPAC in 2016.
11. What is critical size in nuclear chemistry ?
12. Write an example of photonuclear reactions.

(12 × 1 = 12 weightage)

Turn over

Section B

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

13. Explain the following :
- Ammonia is more easily liquefiable than HCl ; and
 - Boiling point of H₂O is higher than that of H₂S.
14. What is meant by Walsh diagram ? Explain with example.
15. Comment of the statement, "All Arrhenius acids are also Bronsted acids but all Arrhenius bases are not Bronsted bases".
16. Identify the conjugate acid base pair in HF dissolved in H₂SO₄.
17. Discuss briefly on the structure and method of preparation of P-S cage compounds.
18. How is sulphur nitrides prepared ? Explain one dimensional metallic character of (SN)_x.
19. Give the structural classification of B₄H₁₀, B₅H₉ and 1, 2 B₁₀C₂H₁₂.
20. What are the products of the following reactions :
- B₄H₁₀ + 2EtO →
 - B₄H₁₀ + 4OH⁻ →
 - B₂H₆ + 2NH₃ →
21. What are Frost diagrams ? To what use are they put ? Explain giving examples.
22. Explain the preparation and structure of isopoly acids of Mo and W.
23. Write a note on neutron activation analysis ?
24. Discuss the importance of radiation dosimetry.

(8 × 2 = 16 weightage)

Section C

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

25. Briefly discuss the following :
- Determination of molecular structure by X-ray diffraction ; and
 - Applications of HSAB concept.

26. (a) Explain the synthesis structure and used of silicones.
(b) Discuss the synthesis, mechanism of formation and uses of chlorocyclophosphazenes
27. Compare the properties of lanthanides and actinides with special reference to magnetic and Spectral properties.
28. Explain the different models of nucleus.

(2 × 4 = 8 weightage)

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**FIRST SEMESTER M.Sc. DEGREE (SUPPLEMENTARY) EXAMINATION
NOVEMBER 2020**

(CUCSS)

Chemistry

CH 1C 01—QUANTUM CHEMISTRY AND GROUP THEORY

(2015 Admissions)

Time : Three Hours

Maximum : 36 Weightage

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

1. What do you mean by stationary state in quantum mechanics ?
2. Choose the acceptable and non acceptable wave functions with the indicated intervals from the list. Justify your answer in each case.
 - a) $e^{-x}(0, \infty)$.
 - b) $e^{-x}(-\infty, \infty)$.
 - c) $\sin^{-1}x(-1, 1)$.
 - d) $(\sin x)/x(0, \infty)$.
 - e) $e^{-|x|}(-\infty, \infty)$.
3. Zero point energy of a rigid rotator is zero. Is this against the uncertainty principle ?
4. Show that $\langle p \rangle = 0$ for all states of a one-dimensional box of length 'a'.
5. Write the Schrodinger equation and Hamiltonian for a particle on a sphere in spherical polar coordinates.
6. Write a note on Kronecker Delta related to wavefunctions.
7. Calculate the energy of an electron in the ground state and first excited state of H atom.
8. Define spin orbital. Write one example.
9. Show that 120° rotation and 240° rotation are conjugate elements of C_{3v} point group ?
10. Define cyclic groups. Give an example.

- Any two irreducible representations are orthogonal. Demonstrate using the character table for C_{2v} point group.
- What is the relation between S_2 and i . Illustrate using an example.

(12 × 1 = 12 weightage)

Part B

Answer any **eight** questions.

Each question carries a weightage of 2.

- Show that Schrodinger wave equation is an Eigenvalue equation.
- Evaluate the commutator $[\hat{x}, P\hat{x}]$. What is the physical significance of a commutator ?
- Explain the postulate of quantum mechanics that consider the average of measurements of an experiment.
- Show that the radial distribution of 2p orbital of hydrogen atom exhibits are maximum at $r = 4a_0$.
- β -carotene is a linear polyene in which 10 single and 11 double bonds are in conjugation along a chain of 22 carbon atoms. If we take each C-C bond length to be about 140 pm, then the length of the molecular box in β -carotene is 2.94 nm. Estimate the wavelength of light absorbed by this molecule from its ground state to next higher excited state.
- Using the first Hermite polynomial expressions show that the vibrational transition from $v = 0$ to $v = 1$ is allowed and from $v = 0$ to $v = 2$ is forbidden.
- The bond length of $^{12}C^{14}N$ is 117 pm and its force constant is 1630 Nm^{-1} . Predict the rotation vibration spectrum of $^{12}C^{14}N$.
- Elaborate on the significance of various quantum numbers. Explain the electron spin postulate and angular momentum with the help of Stern Gerlach experiment.
- Construct the group multiplication table of C_3V Point Group.
- Apply reduction formula to derive a linear combination of irreducible representations from one of the reducible representation of water.
- What do you mean by a group. What are the fundamental properties of a group. Illustrate the fundamental properties using the multiplication of elements of a point group.
- What are the transformation matrices of C_{2v} point group with a set of 3 vectors as basis (Given a vector has 3 components).

(8 × 2 = 16 weightage)

Part C

Answer any **two** questions.

Each question carries a weightage of 4.

- (a) Show that the variables in the Schrödinger equation for a cubic box may be separated and the overall wave functions expressed as $X(x)$. $Y(y)$. $Z(z)$.

- (b) Deduce the energy levels and wave functions,
- (c) Show that the wavefunctions are orthonormal
- (d) What is the degeneracy of the level with $E = 14h^2/8ml^2$.
26. Describe the postulates of quantum mechanics with necessary explanations for each postulates.
27. Explain the principles of Great Orthogonality Theorem and apply the theorem to derive the character table for C_{4v} point group.
28. Explain the systematic determination of the point group of a molecule. Draw the flow chart for the systematic determination of point groups of molecules. Give the differences between cyclic and dihedral point groups with examples.

(2 × 4 = 8 weightage)

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