D 93389 (Pages : 2) Name.....

Reg. No.....

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)

Turn over

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.

$$M_1 \xrightarrow{k_1} R_1 + M_2\,(E_1)$$
$$R_1 + M_1 \xrightarrow{k_2} M_3 + R_2\,(E_2)$$
$$R_2 \xrightarrow{k_3} R_1 + M_4\,(E_3)$$
$$2R_2 \xrightarrow{k_4} (R_2)_2\,(E_4)$$

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)

D 13105 **(Pages : 2)** **Name.....**

Reg. No.....

FIRST SEMESTER M.Sc. DEGREE (REGULAR/SUPPLEMENTARY) EXAMINATION, NOVEMBER 2021

(CBCSS)

Chemistry

CHE1C04—THERMODYNAMICS, KINETICS AND CATALYSIS

(2019 Admission onwards)

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. *The instruction if any, to attend a minimum number of questions from each sub section / sub part / sub division may be ignored.*
4. *There will be an overall ceiling for each Section / Part that is equivalent to the maximum weightage of the Section / Part.*

Section A

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

1. Define chemical potential in terms of : (a) internal energy ; and (b) Helmholtz free energy.
2. One mole of toluene is mixed with 0.5 moles of benzene at 300k to form an ideal solution. Find the free energy of mixing.
3. Distinguish between equilibrium and steady state conditions.
4. State and explain onsager reciprocal rlation.
5. Define secondary salt effect.
6. Unimolecular gas phase reactions follow first order kinetics at high pressures and second order kinetics at low pressures. Why ?
7. Distinguish between activated and non-activated adsorption.
8. Explain 'catalyst poisoning'.

Turn over

9. Define Michaelis-Menton constant. Explain its significance.

10. Nano materials have high surface area. Justify the statement.

(8 × 1 = 8 weightage)

Section B

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

11. Use third law of thermodynamics to show that absolute zero of temperature is unattainable.

12. Define partial molal volume. How is it evaluated ? Discuss.

13. Derive an equation for the rate of entropy production for one component system with heat and matter transport.

14. What are the conditions under which linear relationship exists between force and flux ? What are the advantages of a linear relationship ?

15. Derive an equation to show primary salt effect.

16. Show that for rigid sphere model of bimolecular reactions. Absolute rate theory agrees with simple collision theory.

17. How would you determine pore size distribution of a solid using mercury porosimetry ?

18. Discuss sol-gel method of preparation of catalysts.

(6 × 2 = 12 weightage)

Section C

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

19. Discuss Someroff Herishelwood theory of branching chain reactions.

20. Derive BET adsorption isotherm.

21. Compare Langmuer-Hunshelwood surface catalysed reactions. How would you identify the mechanism under a guess set of conditions ?

22. Define potential energy surface with the help of potential energy surface explain 'reaction co-ordinate' for the process :

$H + F_2 \rightarrow HF + H.$

(2 × 5 = 10 weightage)

D 32671 **(Pages : 2)** **Name.....**

Reg. No.....

FIRST SEMESTER M.Sc. (CBCSS) REGULAR/SUPPLEMENTARY DEGREE EXAMINATION, NOVEMBER 2022

Chemistry

CHE1C01—QUANTUM MECHANICS AND COMPUTATIONAL CHEMISTRY

(2019 Admission onwards)

Time : Three Hours Maximum Weightage : 30

Section A

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

1. Which of the following one well behaved functions :

   (a) e^{x}; (b) e^{ix}; (c) e^{-ax^2}; (d) $\sin^{-1} x$.

2. Explain with example 'conservative system'.

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

4. Explain the term 'Symmetry breaking'.

5. The solutions of a planar rotor are $\frac{1}{\sqrt{\Pi}} e^{im\phi}$. Express it as a real function.

6. 1s wave function for H atom is Ae^{-r/a_0}. Represent the function graphically. Explain.

7. State and explain independent particle model.

8. What do you mean by 'Slater type of orbitals' ? Write one example.

9. Explain the term 'molecular mechanics' in computational chemistry.

10. Write Z-matrix for NH_3.

(8 × 1 = 8)

Section B

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

11. Show that eigen functions of a Hermitian operator are mutually orthogonal.

Turn over

12. Write Rogrigue's formula. Use the formulate to find $H_{(X)}$ for $v = 4$ in simple harmonic oscillator.

13. Find the commutator of $\hat{L}_x$ and $\hat{L}_y$.

14. 1s wave function for H atom is Ae^{-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 Fock's modification of Hartree self consistent field method.

17. Compare semi empirical and abinitio methods of computational chemistry.

18. How do you classify basis sets ? Discuss.

(6 × 2 = 12)

Section C

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

19. Discuss postulates of quantum mechanics.

20. Apply Schrödinger wave equation for a spherical rotor. Find eigen functions and eigen values.

21. Use variation theorem to find the ground state energy of particle in one dimensional box with slanted bottom.

22. (a) Find the ground state energy of He by first order Perturbation method.

    (b) What are the general features of a Gaussian input file ? Discuss.

(2 × 5 = 10)

D 52781 **(Pages : 2)** **Name.....**

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FIRST SEMESTER M.Sc. DEGREE (REGULAR/SUPPLEMENTARY) EXAMINATION, NOVEMBER 2023

(CBCSS)

Chemistry

CHE1C04—THERMODYNAMICS, KINETICS AND CATALYSIS

(2019 Admission onwards)

Time : Three Hours Maximum : 30 Weightage

Section A

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

1. Define chemical potential in terms of u, H, A and G.
2. Define excess thermodynamic functions. What is their significance ?
3. Define phenomenological co-efficient. Explain its significance.
4. State and explain Onsagar reciprocal relation.
5. Explain with example chain branching in kinetics.
6. Distinguish between diffusions controlled and activation controlled reactions.
7. Explain the term 'Steric factor. Explain' in collision theory.
8. Distinguish between activated and non-activated adsorption.
9. Uni-molecular surface catalysed gas phase reactions follow first order kinetics at low pressures and zero order kinetics at high pressures. Why ?
10. Explain with example phase transfer catalysis.

(8 × 1 = 8 weightage)

Section B

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

11. Using third law of thermodynamics. Show that absolute zero of temperature in unattainable.
12. Define fugacity . How is it determined ?
13. Derive an equation for the rate of entropy production for one component system with heat and matter transport.

Turn over

14. Rationalise (a) thermolecular pressure differences ; (b) thermal osmosis using irreversible thermodynamics.

15. Derive Brönsted Bjerrum relationship for the effect of salt on the rate of ionic reactions in solution.

16. The pre exponential term for first order reaction is $5 \times 10^{13} s^{-1}$. Calculate the entropy of activation at 500 k.

17. How would you study pore size distribution of a solid by mercury porosimetry ? Explain.

18. Nano materials in general have very high surface area. Comment on the statement.

(6 × 2 = 12 weightage)

Section C

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

19. Write mechanism for thermal decomposition of acetaldehyde. Derive the rate law.

20. What are the assumptions in Absolute rate theory. Following the theory derive an equation for the rate of bimolecular reaction.

21. Discuss briefly the various theories for oscillating chemical reactions.

22. (a) How would you determine partial molal volume of a component in solution ? Discuss.

    (b) How would you determine absolute entropy of a gas using third law of thermodynamics. Discuss.

(2 × 5 = 10 weightage)