

Reg.	No.	i	 	 	

III Semester M.Sc. Degree (CBSS – Reg./Suppl./Imp.)
Examination, October 2020
(2014 Admission Onwards)
CHEMISTRY

CHE 3C.10: Physical Chemistry - III

Time: 3 Hours

Max. Marks: 60

SECTION - A

Answer all questions in a word or sentence. Each question carries 1 mark. (8×1=8)

- Explain the term 'threshold energy' in collision theory of reaction rates.
- 2. Define relaxation time.
- 3. Distinguish between Arrhenius complex and van't Hoff Complex.
- 4. What is primary salt effect?
- 5. What is surface pressure?
- 6. Explain term KLL with reference to Auger electron Spectroscopy.
- 7. State Hardy-Schultz rule.
- 8. Define isoelectric pH. Commission has province a pagistal audiental and

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Answer eight questions. Answers may be in one or two sentences. Each question carries 2 marks. (8×2=16)

9. Decomposition of NO₂Cl follows the mechanism

$$NO_2CI \xrightarrow{k_1} NO_2 + CI$$

 $NO_2CI + CI \xrightarrow{k_2} NO_2 + CI_2$

Derive the rate law.



- 10. Define enthalpy of activation. How is it related to activation energy for
 - a) first order reaction
- b) second order gas phase reaction?
- 11. How would you follow fast reactions by NMR spectroscopy?
- 12. What is secondary salt effect?
- 13. What is 'cage effect'?
- 14. Write Taft equation. Explain.
- 15. What is the application of LEED in surface analysis?
- 16. Spontaneous adsorption is always exothermic. Why?
- 17. Distinguish between activated and nonactivated adsorption.
- 18. What is stern model of electrical double layer?
- 19. Explain with example micelle.
- 20. What is sedimentation potential?

SECTION - C

Answer four questions. Each question carries 3 marks.

 $(4 \times 3 = 12)$

- 21. Show that for the rigid sphere model of bimolecular reactions Absolute Rate Theory agrees with simple Collision Theory.
- 22. Discuss relaxation method of studying fast reactions.
- Decomposition of acetaldehyde follows the mechanism given below. Derive the rate law.

$$CH_3CHO \xrightarrow{k_1} CH_3 + CHO$$
 $CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO$
 $CH_3CO \xrightarrow{k_3} CH_3 + CO$
 $2 CH_3 \xrightarrow{k_4} C_2H_6$

24. Briefly discuss Michaelis-Menten theory of enzyme catalysis.



- 25. Derive Gibbs adsorption isotherm.
- 26. Write BET adsorption isotherm. Show that it approximates to Langmuir adsorption isotherm under limiting conditions. What is the limiting condition?
- 27. Briefly explain Donnan Membrane equilibrium.
- 28. Derive an equation to show the relationship between diffusion coefficient and molecular size.

SECTION - D

Answer either 'a' or 'b' of each question. Each question carries 6 marks. (4x6=24)

29. a) Discuss Absolute Rate Theory of reaction rates.

OR

- b) What are the drawbacks of Lindemann's theory of unimolecular reactions? How is it modified? Discuss.
- Write mechanism for photochemical reaction between H₂ and Cl₂. Derive the rate law.

OR

- b) i) Compare kinetics of reactions in solution with the kinetics of gas phase reactions.
 - ii) Derive an equation to show the effect of dielectric constant of the medium on the rate of ionic reactions.
- 31. a) What are the methods of determining surface area of solids? Discuss.

OR

b) i) Show that for competitive adsorption of two gases A and B, the fractional surface coverage θ_A for adsorption of gas A is given by

$$\theta_A = \frac{b_A P_A}{1 + b_A P_A + b_B P_B}$$

(P_A and P_B are partial pressures of A and B b_A and b_B are constants)

- ii) Discuss theory and applications of XPS.
- 32. a) Discuss briefly stability of Colloids.

OF

b) Derive an equation for zeta potential from electro osmotic measurements.