Reg. No. : ....

Name : ....

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)**

1. 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.

SECTION – B

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

9. Decomposition of NO_2Cl follows the mechanism

$$NO_2Cl \xrightarrow{k_1} NO_2 + Cl$$
$$NO_2Cl + Cl \xrightarrow{k_2} NO_2 + Cl_2$$

Derive the rate law.

P.T.O.

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.   (4×3=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.

23. 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.   (4×6=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.

30. a) Write mechanism for photochemical reaction between H_2 and Cl_2. 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.

OR

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