International Institute of Information Technology, Hyderabad
Chemical Kinetics and Reaction Dynamics
Final examination - Monsoon 2023

Time: 2 Hrs

Max. marks=50

Answer each question coherently in one place - do not scatter the answer to disjoint sheets.
All symbols have the usual meaning as in the text book followed for the course.
Formulae written on one side of a A4 sheet (no derivations/diagrams) and calculator are allowed.
Evaluation will be based on brief explanation accompanying correct answers.

1. For the reaction A→P with autocatalysis with given initial amounts, find by explicit integration the amount of A and P at a later time. 6

2. The equilibrium constant for the autoprotolysis of water, $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$, is 1.008×10^{-14} at 298 K. After a temperature-jump, the reaction returns to equilibrium with a relaxation time of 37 μs at 298 K and pH ≈ 7. The forward reaction is first-order and the reverse is second-order overall. Calculate the rate constants for the forward and reverse reactions. 8

3. How does the collision-theory explain the activation needed for a reaction? Describe the essential features of the harpoon mechanism and how the steric factor may be calculated for a reactive system using this mechanism. 5 + 4

4. An aminoacid on the surface of an enzyme was labeled covalently with 1.5-I AEDANS and it is known that the active site contains a tryptophan residue. The fluorescence quantum yield of tryptophan decreased by 15% due to quenching by 1.5-I AEDANS (Förster parameter, $R_0 = 2.2$nm). What is the distance between the active site and the surface of the enzyme? 6

5. For gas phase reactions other than unimolecular, show that the pre-exponential factor, $A = e^{-(\Delta n^\ddagger - 1)} \frac{k_B T}{h} e^{\frac{\Delta S^\ddagger}{R}}$ ($\Delta V^\ddagger$ =change in volume for activation, and $\Delta n^\ddagger$ =change in number of moles on activation; you may get a factor of N_A depending on the units you choose). 6

6. (a) Explain briefly the variation of rate constant for Electron transfer between a donor and acceptor in homogeneous systems as different substituents are added to the acceptor. 5

(b) At 300 K, for an electron donor–acceptor pair, $k_{et} = 2.02 \times 10^5 s^{-1}$ for $\Delta_r G^{\ominus} = -0.665 eV$. When a substituent is added to the electron acceptor, these change to $k_{et} = 3.33 \times 10^5 s^{-1}$ and $\Delta_r G^{\ominus} = -0.975 eV$. Assume that the distance between donor and acceptor is the same in both experiments and estimate the value of the reorganisation energy.

(gas constant, $R = 8.63 \times 10^{-5} eV/K$). 4

7. An atom on a metal surface is hit 100 times a second by gas atoms above it. If the temperature is increased to twice its value, how many times will the surface atom hit in a second? 6