International Institute of Information Technology, Hyderabad
Chemical kinetics and Reaction Dynamics - Monsoon 2020
Final examination

Time: 80 **mins** **Max. marks=** 50

Answers on paginated A4 sheets scanned or camera photographed should be submitted before the deadline. Evaluation will be based on brief explanation accompanying correct answers.

Each question carries 10 marks.

1. The rate constants for a gaseous reaction A $\rightarrow$ P are 3.40×10^{-3} **s**$^{-1}$ **and** 4.40×10^{-4} **s**$^{-1}$ **at [A]** $= 4.37 \times 10^{-4}$ **mol dm**$^{-3}$ **and** 1.00×10^{-5} **mol dm**$^{-3}$**, respectively. Use Lindemann–Hinshelwood mechanism to calculate rate constant for the activation step.**

2. For gas phase reactions other than unimolecular, show that the pre-exponential factor, $A = e^{-\left(\Delta n^{\ddagger}-1\right)} \frac{k_B T}{h} e^{\frac{\Delta S^{\ddagger}}{R}}$ **(** $\Delta V^{\ddagger}$ **=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).**

3. Use the following data for calculating the rate constant for the reaction H+HBr$\longrightarrow$H$_2$+Br :

Difference between zero-point energy levels of activated complexes and reactants= 5.0**kJmol**$^{-1}$

HBr internuclear distance = 141.4 **pm**

HBr vibrational frequency = 2650**cm**$^{-1}$

Activated complex is linear with H-H distance= 150 **pm and H-Br distance=** 142 **pm**

The real vibrational frequencies in the activated state are 2340 **(non-degenerate) and** 260 **cm**$^{-1}$ **(two degenerate bending ones). The fourth frequency corresponds to passage over the barrier.**

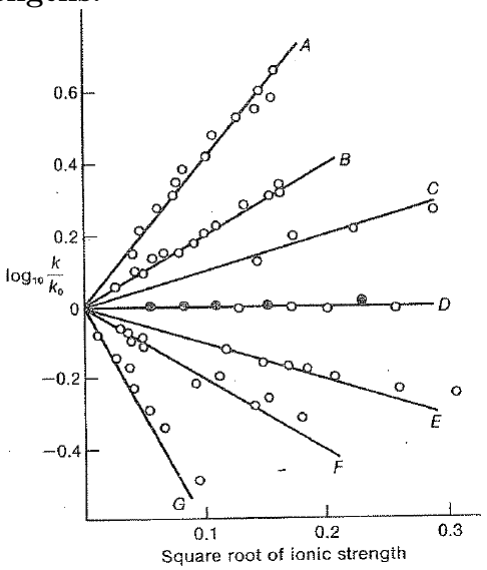
To calculate the moment of inertia of the activated complex you need to use the lever principle - If C.M. is at a distance r_i **(negative if left and positive if right of C.M.) from mass** m_i**, then** $\sum_i m_i r_i = 0$**.**

Find atomic distances and then moment of inertia for the activated complex.

Then find the partition functions of the reactants and the activated complex using standard values of constants, etc., and then find the rate constant.

(contd. on next page)

4. Shown below is a plot of logarithm of rate constants a function of square root of ionic strengths:



Which of the five labels A-G are suitable for the following reactions :

(i) $\mathbf{S_2O_8^{2-}+I^-}$

(ii) $\mathbf{Fe^{2+}+Co(C_2O_4)_3^{3-}}$

5. (i) An atom on a metal surface is hit 100 times a second by gas atoms above it. If the temperature is increased to four times its value, how many times will the surface atom be hit in a second?

(ii) Do both the diffusion-controlled reaction and the activation-controlled reaction have activation energies?