ChE631A: Mid Semester Exam (Max. Marks 90)

Dated: September 22, 2024 (Time : 2hrs)

Name: ____________ **Roll No.:**____________ **Signature:**____________

Points to Keep in Mind

1. You are expected to abide by highest standards of academic honesty. You have been apprised of it during the first lecture. Needless to say, if you are caught copying you get only one grade, i.e., **F**.
2. State the assumptions made clearly.
3. Any answer (or graph labels) without units has no meaning. There will be points deducted for it.
4. One A4 size sheet with formulae and calculator is allowed.
5. *Above all, read the question carefully.*

Good Luck 🙂🙂🙂

Session I (1hr 50mins)

1. [20 points] **Affect of Poisoning on Catalyst Effectiveness Factors:**

   In a commercial heterogeneous catalytic reactors, the activity of the catalyst usually changes with time. In this problem we will consider a poisoned pore and derive an effectiveness factor for the poisoned pore. Assume the poisoning follows separable kinetics and decreases the total number of sites or the fraction of the total active surface area homogeneously. This is indeed the case when the poisoning reaction is slow relative to the diffusion of the poison.

   Assume the rate of poisoning is extremely slow compared to the overall reaction rate and pseudo-steady state can be applied to derive an expression for rates. At any instant, let the fraction of the surface that is poisoned is given by α. Derive an expression for the Thiele modulus and effectiveness factor (poisoned) for an idealized cylindrical pore, which has been homogeneously poisoned.

   Assume that the reaction is taking place on the pore wall and is first-order (neglect adsorption/desorption steps). No reaction takes place at the pore end and isothermal-isobaric conditions are maintained inside the pore. Also, assume there are no radial gradients of concentration. Apply mole balance on a small element (a thickness of Δx) along the length of the pore and develop a non-dimensionalized differential equation. To earn full points you will need to mention the boundary conditions with proper justification and provide an analytical solution for the second-order differential equation.

   Also, obtain the factor, Υ, for the poisoned pore

   $$\Upsilon = \frac{-r''_{\text{poisoned}}(\text{obs})}{-r''_{\text{unpoisoned}}(\text{obs})} \tag{1}$$

   Here, rates are defined per surface area of the catalyst. Obtain the limits of this number for small and large values of Thiele modulus.

2. [10 points] You are given data for the following two cases in a spherical pellet. Assume the reaction is first-order and adsorption/desorption steps can be neglected. Will departure from isothermal behaviour be important in any of the two cases?

(a) Enthalpy of reaction, $\Delta H_{\text{rxn}} = -80$ kJ/mol.
Effective Diffusivity, $D_e = 10^{-1}$ cm^2/s.
Concentration of reactant at the pellet surface, $C_{As} = 4 \times 10^{-5}$ moles/cm^3.
Effective Conductivity, $k_e = 16 \times 10^{-4}$ J/(cm-s-°C).

(b) Enthalpy of reaction, $\Delta H_{\text{rxn}} = -50$ kJ/mol.
Effective Diffusivity, $D_e = 10^{-2}$ cm^2/s.
Concentration of reactant at the pellet surface, $C_{As} = 4 \times 10^{-4}$ moles/cm^3.
Effective Conductivity, $k_e = 16 \times 10^{-3}$ J/(cm-s-°C).

3. [30 points] Following data is obtained for alkylation of ethylbenzene with light olefins (ethylene and propylene) in zeolite Y catalyst in a fixed-bed reactor. The reaction is accomplished at 463 K and 25 bar and is carried in excess of ethylbenzene. At these conditions, the reaction can be assumed to be pseudo-first-order with respect to the olefin. The catalyst pellets have uniform pore size, the porosity of the catalyst is 0.5 and the tortuosity is 5.0. The density of the pellets is 1000 kg/m^3. The observed rate [$-r'$(obs)] and rate constant [k'(obs) = $\Omega k'$] were measured for two different catalyst pellet sizes. Here Ω is the overall effectiveness factor. Relevant results are given below:

Radius of Pellet (R_p,mm)	**Film Mass Transfer Coefficient, (k_c, m/s)**	**External Surface Area of Catalyst, S_p (m^2/kg)**	**$-r'$(obs) [mol/g-s]**	**k'(obs) [m^3/g-s]**
0.17	1.07×10^{-3}	17.13	11.7×10^{-6}	1.06×10^{-6}

(a) Determine whether or not internal mass transfer limitations are significantt. Assume the diffusivity of olefins in ethylbenze is $D_{AB} = 1.9 \times 10^{-4}$ cm^2/s.

(b) Calculate the Thiele modulus and internal effectiveness factor.

(c) Determine the overall effectiveness factor. Make suitable assumptions, if necessary.

4. [20 points] The theorist in the company XXX has proposed the following mechanism for the thermal decomposition of acetone.

- **Initiation:**
  $CH_3COCH_3 + CH_3COCH_3 \xrightarrow{k_1} CH_3COCH_3 + CH_3\cdot + CH_3CO\cdot \quad E_a = 84$ kcal/mol
  $CH_3CO\cdot \xrightarrow{k_2} CH_3\cdot + CO \quad E_a = 10$ kcal/mol
- **Propagation:**
  $CH_3\cdot + CH_3COCH_3 \xrightarrow{k_3} CH_4 + CH_3COCH_2\cdot \quad E_a = 15$ kcal/mol
  $CH_3COCH_2\cdot \xrightarrow{k_4} CH_3\cdot + CH_2CO \quad E_a = 48$ kcal/mol
- **Termination:**
  $CH_3\cdot + CH_3COCH_2\cdot \xrightarrow{k_5} C_2H_5COCH_3 \quad E_a = 5$ kcal/mol

(a) Using pseudo-steady state approximation to come up with a rate expression in terms of the individual rate constants and concentrations of the stable species. Make suitable assumptions to simplify the model with proper justification. [HINT: Use magnitude of activation energies and concentration of reactive intermediates for simplifying the rate expression.]

(b) What is the overall order and apparent activation energy?

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Session II (10mins)

5. **True or False**
   Note: True means "always correct" and False means "not true"

   (a) [1 point] Transition state theory assumes that there is no-recrossing of reacting molecules, and therefore, gives the lower limit of the rate coefficient.

   (b) [1 point] The step which has the highest barrier is the only rate-determining step.

   (c) [1 point] For a reaction conducted in a batch reactor in an isothermal-isobaric conditions, the equilibrium conversions gives the maximum yield of the products.

   (d) [1 point] Presence of an inert increases the equilibrium conversion of the gas-phase reaction.

   (e) [1 point] Surface reaction is always the rate limiting step at low temperatures.

   (f) [1 point] Adsorption is an exothermic reaction.

   (g) [1 point] Langmuir adsorption isotherm assumes that there is no interaction between the adsorbates.

   (h) [1 point] Steady-state implies implicitly that the surface concentration of the species is low.

   (i) [1 point] Apparent activation energy is always positive.

   (j) [1 point] Knudsen diffusion coefficient does not depend on pressure.