10.37 Exam 2 25 April, 2007
100 points

Problem 1: 35 points

A protein and ligand bind reversibly with $K_d = 10$ nM . The association rate constant $k_{on} = 2\text{x}10^4 M^{-1}s^{-1}$. The two species are mixed at an initial protein concentration of 3 nM and an initial ligand concentration of 0.2 nM.

a) At equilibrium, what fraction of the ligand will be complexed with protein? (15 points)

b) At what time will the fraction of ligand in complex reach 95% of the equilibrium value? (20 points)

Justify any assumptions you make to simplify equations.

Problem 2: 30 points

A surface-catalyzed reaction follows Rideal-Eley kinetics as follows:

$$A + S \underset{k_{-A}}{\overset{k_A}{\rightleftarrows}} AS$$

$$AS + A \xrightarrow{k_1} A_2 + S$$

Where *A* and A_2 are in the gas phase, *S* is a reactive site on the surface, and *AS* is a molecule of *A* adsorbed to a reactive site.

Assuming that:

adsorption of *A* is at rapid equilibrium
reaction of *AS* with *A* is rate-limiting
desorption of A_2 is very rapid

Derive the steady-state rate law for production of A_2 as a function of the concentration of A and the total initial reactive site density S_o .

Problem 3: 35 points

It is desired to make a product X-Y via this reaction:

X-OH + Y-H → X-Y + H_2O

An equimolar feed of liquid X-OH and Y-H at 25°C are fed to a CSTR. At 25°C, where all 4 material species are liquids, the heat of reaction ΔH_{rxn}=-200 kJ/mole, and the heat capacity of each liquid-phase species is 4 kJ/(kg C°). The molecular weight of X-OH is 150 g/mole, and the molecular weight of Y-H is 100 g/mole. The temperature inside the reactor (T) is controlled by putting the reactor in thermal contact with a fluid flowing over the outside of the reactor at temperature T_a. To a good approximation, the heat transfer rate (Q, in watts) from the fluid flowing over the outside the reactor to the contents of the reactor is given by the linear expression: $Q = UA(T_a - T)$

a) If the reaction is carried out with the reactor at steady-state at the inlet temperature of 25°C, is T greater than, less than, or equal to T_a? (5 points)

b) When running the reactor at T = 25°C to 50% conversion, the productivity is unacceptably low. To try to accelerate the reaction, it is decided to increase the steady-state reactor temperature to T = 105°C. At this temperature, all of the H_2O formed evaporates, but the other species are still liquids. The heat of vaporization of H_2O at 105°C is +40 kJ/mole. When T=105°C, the reaction runs to 50% conversion 10x faster than it did at 25°C, so we increase the flowrates until the reactor is making 10x as much product as it did at 25°C (still at 50% conversion). When we achieve the new steady-state high-productivity operation at 105°C, will the magnitude of Q (i.e. |Q|) be larger, smaller, or the same as it was when we were operating at 25°C? At this steady-state condition, is T greater than, less than, or equal to T_a? (20 points)

c) Since operating hot improved our productivity, but conversion is still pretty low, the operator tries to improve things by cranking up the temperature, preheating the inlet streams to 185°C and increasing T_a. For good measure the operator simultaneously cranks up the reactor pressure from 1 bar to 100 bar; at this high pressure all the species remain as liquids. (The reactor is safe at this condition, and even up T = 300°C.) Curiously, the conversion and productivity of the reactor do not increase under these severe conditions, instead they decrease. Propose an explanation for this experimental observation. (5 points)

d) Your manager gives the operator who turned up the temperature (without doing any calculations first) a formal reprimand, saying the operator is probably lucky that the conversion went down instead of increasing. Why do you think the manager was happy that conversion was low instead of increasing a lot? (5 points)