Problem 1. (100 points) A reactant stream is split to feed, in parallel, two CSTRs, one of which is twice the volume of the other. The effluents from the two CSTRs are combined. The reaction of interest follows a first-order rate law.

a) (50 points). How should the feed stream be split in order to maximize the total reactant conversion in the combined effluent from the two CSTRs?

b) (50 points). Using the same feed, what overall conversion would be obtained by placing these same two CSTRs in series (i.e. the effluent of the first is the feed of the second)? (Consider both possible topologies – one where the large CSTR feeds the smaller, and one where the small CSTR feeds the larger.) Is this conversion superior or inferior to the best case calculated in a)?
Problem 2. (100 points) An appealing partial solution to the greenhouse gas problem is to convert biomass into liquid fuels. Most of biomass is composed of linked C6 sugars (C₆H₁₂O₆) and C5 sugars (C₅H₁₀O₅), which can be broken down by an enzyme secreted by fungi. Ideally, the sugars could then be converted into ethanol or other liquids in subsequent reactions.

This mechanism is proposed for the enzymatic breakdown:

\[
\text{C}_{11}\text{H}_{22}\text{O}_{11} + \text{Enzyme } \rightarrow \text{Complex} \quad \text{(reaction 1)}
\]

\[
\text{Complex } \rightarrow \text{Enzyme} + \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_5\text{H}_{10}\text{O}_5 \quad \text{(reaction 2)}
\]

Reaction 1 is expected to be reversible under some conditions, but reaction 2 is expected to be irreversible.

Experimental rate data on this enzyme from low-conversion batch-reactor experiments can be fit to this expression:

\[
\frac{d[C_5H_{10}O_5]}{dt} = r = \frac{a[C_{11}H_{22}O_{11}]_0[\text{Enzyme}]_0}{1 + b*[C_{11}H_{22}O_{11}]_0} \quad \text{(Eqn 3)}
\]

\[
a = 2 \times 10^4 \text{ liter/mole-second} \quad b=10^8 \text{ liter/mole.}
\]

where \([C_{11}H_{22}O_{11}]_0\) and \([\text{Enzyme}]_0\) are the initial concentrations added to the mixture, i.e. (moles added / volume of solution), not necessarily the actual concentrations of these species in the beaker when the reaction is running, since some of the enzyme will exist in the form of the complex.

(a) (20 points) Is the observed rate law (Eqn 3) consistent with the mechanism shown above? If so, give an expression for \(b\) in terms of \(k_1\), \(k_{-1}\), and \(k_2\). If not consistent, explain.

(b) (30 points) Write an equation for the Thiele modulus for this system, as a function of \([C_{11}H_{22}O_{11}]\). Over what range of \([C_{11}H_{22}O_{11}]\) is it reasonable to neglect diffusive transport limitations?

(c) (30 points) If \([C_{11}H_{22}O_{11}]\) is always in the range where transport limitations are negligible, what differential equation(s) should be solved to compute the conversion? What Matlab program would you use to solve the equation(s) numerically? Write the differential equation(s) in the form \(dY/dt = F(Y)\) required by the Matlab solvers.

(d) (20 points) Write (but do not attempt to solve) the differential equation(s) with boundary conditions that would have to be solved to compute the effectiveness factor \(\Omega\) if \([C_{11}H_{22}O_{11}]_{\text{bulk}}\) had a value outside the range specified in part (b). Are you missing any data needed to calculate \(\Omega\)?
**Problem 3. (100 points)** A biosensor experiment is performed with a small amount of immobilized protein and flowing soluble ligand. The observed rate constant during the association phase, and the signal output at equilibrium, are given as a function of ligand concentration in the table below. The equilibrium signal $R_{U_{eq}}$ is proportional to the concentration of protein/ligand complex at the surface. During the association phase the signal follows the following function: $RU = R_{U_{eq}} (1 - e^{-k_{obs}t})$.

<table>
<thead>
<tr>
<th>$[L]_0$ (nM)</th>
<th>$k_{obs}$ (s$^{-1}$)</th>
<th>$R_{U_{eq}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.14</td>
<td>0.00177</td>
<td>1.63</td>
</tr>
<tr>
<td>0.84</td>
<td>0.00186</td>
<td>9.34</td>
</tr>
<tr>
<td>2.1</td>
<td>0.00201</td>
<td>21.5</td>
</tr>
<tr>
<td>5.60</td>
<td>0.00245</td>
<td>47.1</td>
</tr>
<tr>
<td>14.00</td>
<td>0.00350</td>
<td>82.5</td>
</tr>
<tr>
<td>35.0</td>
<td>0.00612</td>
<td>118</td>
</tr>
<tr>
<td>84.00</td>
<td>0.0122</td>
<td>141</td>
</tr>
<tr>
<td>210.00</td>
<td>0.0280</td>
<td>155</td>
</tr>
<tr>
<td>560.00</td>
<td>0.0718</td>
<td>161</td>
</tr>
<tr>
<td>1400.00</td>
<td>0.177</td>
<td>163</td>
</tr>
</tbody>
</table>

A) (60 points) Determine $K_d$, $k_{on}$, and $k_{off}$. Are these data self-consistent?

B) (40 points) In a separate experiment, soluble protein (2 nM) and ligand (0.1 nM) are mixed. At equilibrium, what fraction of ligand is complexed with the protein? At what time following mixing will 95% of this equilibrium value be attained?

**Problem 4. (100 points total)** “Clean Coal” technology is based on first converting the coal into syngas (an $H_2 + CO$ mixture). The syngas can then be purified and used to make clean synthetic fuels, or to generate electricity (with $CO_2$ sequestration). The largest and most expensive reactor in a “clean coal” plant is the gasifier. The main reactions are:

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad \text{(Reaction 1)} \quad \Delta H_{rxn1} = -110 \text{kJ/mole}$$

$$r_1 = k_1(T)[O_2]^2[H_2]/([H_2O] + a[H_2])$$

$$k_1(T) = (10^7 \text{ liter/mole-s})\exp(-2000/T) \quad a = 0.0113 \exp(10000/T)$$

$$C(s) + H_2O(g) \rightarrow H_2(g) + CO(g) \quad \text{(Reaction 2)} \quad \Delta H_{rxn2} = +130 \text{kJ/mole}$$

$$r_2 = k_2[O_2][H_2O]/([H_2O] + a[H_2])$$

$$k_2 = 5 \times 10^4 \text{ s}^{-1} \quad a = 100 \quad \text{at } T=1100 \text{ K}$$

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Problem 4 (continued) The peculiar-looking rate laws come from a quasi-steady-state-approximation treatment of the radicals which are the reactive intermediates in these reactions. Reaction 1 is much faster than reaction 2 at low T, so the gasifier system can be modeled as an adiabatic PFR (volume $V_1$) where most of the $O_2$ is consumed but the $H_2$ formation is negligible, followed by an isothermal CSTR (volume $V_2$) where both reactions occur.

![Gasifier Diagram]

The final 1100 K output stream coming out of the gasifier has no carbon and a negligible concentration of $O_2(g)$, but large concentrations of CO, $H_2$, and steam. Assume that the heat capacity of the feed stream is 3 MJ/ton-Kelvin and that the heat capacity per ton does not change significantly with temperature or the change in composition through the reactions. The process is carried out at $P_{\text{total}}=40$ bar. The input stream is at 700 K, and consists of 120 tons per hour of C(s), 120 tons per hour of steam, 64 tons per hour of $O_2$, and 0.02 tons per hour of $H_2$.

(a) (20 points) What is the molar flow rate of CO, $H_2$, and $H_2O$ at the output? What is the volumetric flow rate of the output?

(b) (25 points) How much heat must be transferred per second to maintain the output at 1100 K? Is the heat flowing into or out of the reactor? How could you adjust the composition of the feed to reduce the amount of heat transfer required, while still maintaining the same Carbon feed rate and output temperature?

(c) (30 points) Write the equation(s) that should be solved to compute the conversion of $O_2$ in the adiabatic PFR, $V_1=1 \text{ m}^3$, in a form that can be solved numerically by Matlab. What Matlab program would you use to solve these equations?

(d) (25 points) What CSTR reactor size $V_2$ is required so that 99% of the initial feed $O_2$ and 99% of the initial feed carbon will be consumed by the time the mixture leaves the isothermal (1100 K) CSTR? Hint: How much carbon was consumed by reacting with $O_2$? So how much carbon must be consumed by reaction 2?