Chemical Reaction Engineering—Homework #4
Due: Online submission on Canvas, **Wednesday, February 12, 2020 at 11:59pm.**
No late submissions will be accepted.

Problems that require a numeric answer should have 3 significant figures.
Units, where required, are shown in blue. Please use these units.

Problem 1: Ozone depletion

Stratospheric ozone (O_3) absorbs UV radiation from the sun, preventing it from reaction the surface of the Earth. Consequently, the loss of this protective layer is a serious environmental concern. You wish to study the chlorine-catalyzed decomposition of ozone in the laboratory. The overall reaction is hypothesized to proceed by the following elementary steps:

Initiation:	$Cl_2 + O_3 \rightarrow ClO + ClO_2$	with rate constant k_1
Propagation:	$ClO_2 + O_3 \rightarrow ClO_3 + O_2$	with rate constant k_2
Propagation:	$ClO_3 + O_3 \rightarrow ClO_2 + 2O_2$	with rate constant k_3
Termination:	$ClO_3 + ClO_3 \rightarrow Cl_2 + 3O_2$	with rate constant k_4
Termination:	$ClO + ClO \rightarrow Cl_2 + O_2$	with rate constant k_5

Given that ClO, ClO_2, and ClO_3 are active intermediates, use the PSSH to derive the rate at which O_3 is depleted as a function of the concentrations of O_2, Cl_2, and/or O_3. No reactive intermediates should appear in your final expression. Assume that the stoichiometric numbers on each step are 1.

Problem 2

2A + B $\rightarrow$ 2C occurs via the elementary-step sequence of reactions shown below. Intermediate I is a reactive intermediate.

$$A + B \overset{k_1,k_{-1}}{\Longleftrightarrow} I$$
$$A + I \overset{k_2}{\rightarrow} 2C$$

a) Derive a meaningful expression (one with no reactive intermediates) for the rate of consumption of A.
b) Using rate symbols to notate each of the above elementary steps, draw an arrow diagram for the mechanism proposed for this reaction, showing the net rate of reaction relatively by the length of the arrows.
c) Assume QE on the first step and repeat parts a) and b) above using this assumption.

d) What is the rigorous justification for QE on the first step? This is the same as asking when would the general PSSH result reduce to the particular QE expression in part C.

Problem 3

The gas-phase reaction $4A \rightarrow 3B + 2C$ occurs via the following sequence of elementary steps. Y and Z are reactive intermediates.

$$A \overset{k_1,k_{-1}}{\Longleftrightarrow} Y + B$$

$$A + Y \overset{k_2}{\rightarrow} 2Z$$

$$Y + Z \overset{k_3}{\rightarrow} C$$

a) Obtain an expression for the reaction rate, r, in terms of the reaction rate for step 3, r_3. Note that the elementary steps written may need to occur multiple times to give the overall reaction stoichiometry.

b) Using your answer from part A, obtain an expression for the reaction rate, r, in terms of rate constants and concentrations of reactants and products, assuming only PSSH on the intermediates.

c) Experimentally, at some conditions, the reaction rate exhibits the following dependence on the concentration of A and B:

$$r = \alpha \frac{(A)^2}{(B)}$$

What approximations are required in the rate expression obtained in part B in order to explain the concentration dependence on this rate?

d) For the general case, simplify the rate expression obtained in part B assuming that:
(i) Step 1 is irreversible.
(ii) Step 1 is quasi-equilibrated.

Problem 4: Pyrolysis of acetaldehyde

The pyrolysis of acetaldehyde is believed to occur according to the following reaction sequence. Assume that all stoichiometric numbers equal 1.

$$CH_3CHO \xrightarrow{k_1} CH_3\cdot + CHO\cdot$$
$$CH_3\cdot + CH_3CHO \xrightarrow{k_2} CH_3\cdot + CO + CH_4$$
$$CHO\cdot + CH_3CHO \xrightarrow{k_3} CH_3\cdot + 2CO + H_2$$
$$2CH_3\cdot \xrightarrow{k_4} C_2H_6$$

a) Derive the rate expression for the rate of disappearance of acetaldehyde, $-r_{AC}$, clearly stating any necessary reasonable assumptions along the way.

b) Under what conditions would your rate expression $-r_{AC}$ reduce to
$-r_{AC} = k(AC)^{\frac{3}{2}}$ where $k = k_2\sqrt{\frac{k_1}{k_4}}$?

c) Write a set of differential equations for the concentrations of AC, C_2H_6, CH_4 and CO based on your rate expression in part A, assuming that the reaction is occurring in an isothermal batch reactor in the gas phase at constant volume.

Problem 5: Comparing QE and PSSH

Consider the following mechanism for the overall reaction: $3A \Leftrightarrow 2C$:

$2A \Leftrightarrow B$; k_1, k_{-1}

$A + B \Leftrightarrow 2C$; k_2, k_{-2}

a) Determine the stoichiometric number for each elementary step in the mechanism.

b) Using the PSSH, derive an expression for d(C)/dt.

c) Assume that step 1 is QE, and now derive an expression for d(C)/dt.