NAME: ______________________________________

Instructions: The exam is closed book and closed notes. Write your name on the exam. Work all the problems. You have 2 hours. Hand in your exam as well as your solution at the end.

Problem 1. Hydrogenolysis of methyltetrahydrofurane. 45 pts.

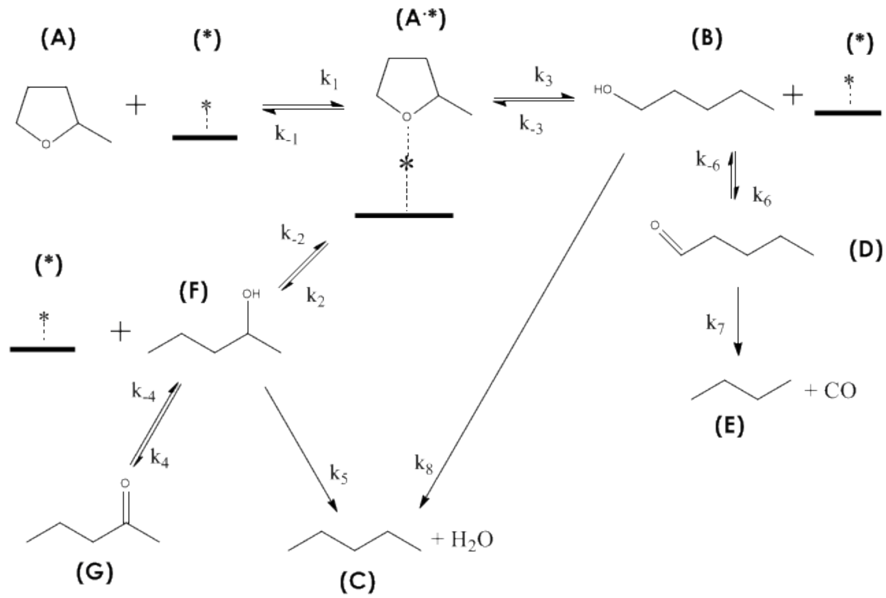

Figure 1: Mechanism for hydrogenolysis of methyltetrahydrofurane on platinum. The H_2 are not shown in the diagram for clarity but are listed in the mechanism below.

Consider the reaction mechanism depicted in Figure 1 consisting of the following reactions [1]

$$A + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A \cdot X \qquad \text{(fast)} \tag{1}$$

$$A \cdot X + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} F + X \tag{2}$$

$$A \cdot X + H_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} B + X \tag{3}$$

$$G + H_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} F \qquad \text{(fast)} \tag{4}$$

$$H_2 + F \xrightarrow{k_5} C + H_2O \tag{5}$$

$$B \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} D + H_2 \tag{6}$$

$$D \xrightarrow{k_7} E + CO \tag{7}$$

$$H_2 + B \xrightarrow{k_8} C + H_2O \tag{8}$$

species	A	A·X	G	F	B	D	E	C	H_2O	H_2	CO
mole percent	20	0	23	2	0	0	10	14	14	7	10

Table 1: Steady-state gas-phase mole percentages at 545 K, 1.3 bar in the effluent of a flow reactor. Adsorbed methyl THF (A·X) is adsorbed on the catalyst and is not present in the effluent, but is present in the reactor in non-negligible amount.

The rates of reactions 1 and 4 are known to be fast, so these two reactions may be assumed to be at equilibrium with respect to the other six reactions. A gas-phase CSTR containing a platinum catalyst is used to collect data. The feed consists of A and H_2. Typical steady-state concentrations of the gas-phase species in the effluent are listed in the table.

(a) From the table, what species are good candidates for making the quasi-steady-state assumption in order to simplify the reaction mechanism. Explain your choice.

(b) Apply the QSSA to these species and the equilibrium assumption to reactions 1 and 4 and express the production rate of butane (E) in terms of reactants and products present in large concentration in the gas phase (greater than 5 mole percent).

(c) Find the production rate of n-pentane (C) in terms of reactants and products present in large concentration in the gas phase (greater than 5 mole percent).

References

[1] U. Gennari, R. Kramer, and H.L. Gruber. Hydrogenolysis of methyltetrahydrofurane on platinum. *Applied Catalysis*, 11:341–351, 1984.

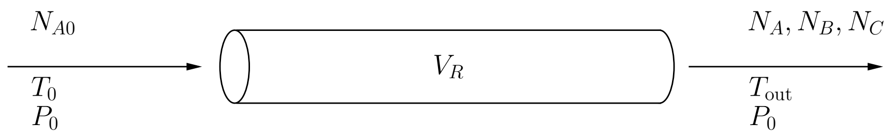

Figure 2: PFR with nonconstant number of moles and nonconstant temperature.

Problem 2. PFR with changing flowrate. 55 points

Consider the gas-phase PFR depicted in Figure 2 in which the following reaction takes place

$$\text{A} \longrightarrow \text{B} + \text{C} \qquad r = kc_A$$

The feed is pure A with molar flow N_{A0} at temperature T_0, pressure P_0 and volumetric flowrate Q_0. The outlet of the reactor is at temperature T_{out}. Neglect pressure drop in the tube ($P = P_0$). The gas may be assumed to be an ideal gas over this temperatures range at this pressure. The rate constant may be assumed independent of temperature over the temperature range $T_0 \leq T \leq T_{\text{out}}$.

(a) List the ideal gas equation of state relating temperature T, pressure P and total molar concentration c?

(b) What is the relationship between total molar flow N, volumetric flowrate Q, temperature T, and pressure P for the ideal gas equation of state?

(c) For this reaction stoichiometry, what is the total molar molar flow N expressed solely in terms of the molar flowrate of component A N_A, i.e. an expression not involving N_B and N_C?

(d) Assume first that the volumetric flowrate does not depend on the change in the number of moles with reaction, nor on the temperature, i.e. $Q(V) = Q_0$. Find the reactor volume, V_R, required to achieve 90% conversion of A. Call this volume V_{R1}. It should be in terms of k, R, T_0, P_0, N_{A0} and the chosen conversion (or N_A at the outlet).

(e) Assume next that the tube is isothermal, but account for the change in volumetric flowrate due to change in the number of moles with reaction. What reactor volume is required to achieve 90% conversion? Call this volume V_{R2}. Find the ratio V_{R2}/V_{R1}. You can obtain a numerical value for this ratio with the given information. Which reactor is larger, V_{R1} or V_{R2}? Why?

(f) Finally, assume the change in temperature is well approximated by the linear relationship

$$T(V) = T_0 + (T_{\text{out}} - T_0)\frac{V}{V_R}$$

Solve the problem again accounting for both the change in temperature and the change in the number of moles with reaction. Assume the reactor temperature at the outlet is one and a half times the temperature at the inlet

$$T_{\text{out}} = 1.5\, T_0 \qquad \text{for } T \text{ in absolute temperature units}$$

What reactor volume is required to achieve 90% conversion? Call this volume V_{R3}. Find the ratio V_{R3}/V_{R2}. You can obtain a numerical value for this ratio with the given information. Which reactor is larger, V_{R2} or V_{R3}? Why?

(g) For this stoichiometry, conversion and temperature change, which effect has more impact on the reactor size, changing the number of moles by reaction or changing the temperature of the gas?