ChE 142 April 11, 2005

Midterm II

(Closed Book and notes, two 8.5”x11” sheet of notes is allowed)

Printed Name ______KEY______________________________

By signing this sheet, you agree to adhere to the U.C. Berkeley Honor Code

Signed Name_______KEY______________________________

1)__10__/10

2)__10__/10

3)__10__/10

4)__20__/20

5)__30__/30

Total: __80__/80

1. (10 Pts.) The rate law for the irreversible reaction A → B + C is known to be as follows: $r_A = -k/C_A$. In an experiment, the concentration of A was monitored as a function of time in a constant volume BSTR.

   a) Which technique would you use to find the rate constant, k? (4 pts.)

   Integral method ***since the form of the rate law is known***

   OR Differential method*, though this method is less appropriate*

   b) How would you find the value of k graphically? (6 pts.)

   Integral method*: we first integrate the rate law* $\frac{dC_A}{dt} = \frac{-k}{C_A}$ => $\int C_A\, dC_A = -k\int dt$.

   The boundary condition is $C_A = C_{A0}$ ***at*** $t=0$.

   Thus, $\frac{1}{2}C_A^2 - \frac{1}{2}C_{Ao}^2 = -kt$. ***So we need to plot*** $\frac{1}{2}C_A^2$ ***vs. t in order to find k from the slope (k = - slope).***

   Differential method*: First, we would need to calculate* $\frac{dC_A}{dt}$, ***which can be calculated from a plot of*** C_A ***vs. t using an appropriate technique. Next, plot*** $\ln\left(-\frac{dC_A}{dt}\right)$ ***vs.*** $\ln(C_A)$***. The intercept would give us k (k=exp(intercept).***

2. (10 Pts.) The irreversible gas-phase reaction of SO_2 to SO_3 is to be carried out in a PFR at a pressure of 10 atm. The inlet feed includes a 50-fold stoichiometric excess of O_2 to assure complete conversion of SO_2. The inlet flow rate is 50 m^3/min and the temperature is 800K.

   $$SO_2 + \tfrac{1}{2} O_2 \rightarrow SO_3$$

   a) You are given data on the partial pressure of product, p_{SO_3}, along the length of the reactor. How would you plot this data to obtain the reaction order with respect to SO_2? Be specific as to exactly what you would plot and how you would plot it. (6 pts.)

   1. ***Design equation: this is a PFR:*** $F_{SO2,0}\frac{dX}{dV} = -r_{SO2}$ ***(SO_2 is limiting reagent)***
   2. ***Rate law: propose a general rate expression:*** $-r_{SO2} = k' P_{SO2}^{\alpha} P_{O2}^{\beta}$
      However, O_2 is in large excess, so we can assume $P_{O2}=P_{O2,0}$
      Therefore, $-r_{SO2} = kP_{SO2}^{\alpha}$, ***where*** $k = k' P_{O2,0}^{\beta}$
   3. ***Stoichiometry:*** $P_{SO2} = P_{SO2,0}(1-X)$; $P_{SO3} = P_{SO2,0}*X$

(This assumes that the volumetric flow rate is approx. constant, which is appropriate since oxygen is in such excess, i.e. the expansion factor, ε, is negligible ($\varepsilon = y_{SO2}\delta = \frac{1}{1+25}\left(1-1-\frac{1}{2}\right) \cong -0.02$***).***

Therefore, $P_{SO2} = P_{SO2,0} - P_{SO3}$ ***and*** $X = (P_{SO2,0} - P_{SO2})/ P_{SO2,0}$

4. ***Combine:*** $-\frac{dP_{SO2}}{dz} = \frac{A_c\, P_{SO2,0}}{F_{SO2,0}}\, k\left(P_{SO2,0} - P_{SO3}\right)^{\alpha} = \frac{dP_{SO3}}{dz}$ ***where*** $V = z * A_c$

5. ***Plot:*** $\ln\left(\frac{dP_{SO3}}{dz}\right)$ versus $\ln\left(P_{SO2,0} - P_{SO3}\right)$ ***based on the following equation:***

$$\ln\left(\frac{dP_{SO3}}{dz}\right) = \ln\left(\frac{A_c\, P_{SO2,0}}{F_{SO2,0}}\, k\right) + \alpha \ln\left(P_{SO2,0} - P_{SO3}\right).$$

The slope of the line will be the order of the reaction, α. ($\frac{dP_{SO3}}{dz}$ ***can be found from a plot of*** P_{SO3} ***versus z).***

b) How would you propose to determine the reaction order with respect to O_2? Would this require additional data, and if so, what data would be needed? (4 pts.)

There are a numerous possibilities, including:

1) ***Method of excess using excess*** SO_2***; need data for*** P_{SO3} ***versus L.***
2) ***Stoichiometric feed and data for*** P_{SO3} ***versus L.***
3) ***Ratio of initial rates with feeds having different values of*** $P_{SO2,0}$***; data for*** P_{SO3} ***versus L.***
4) ***Method of non-linear least squares and data for*** P_{O2}***,*** P_{SO2} ***and/or*** P_{SO3} ***versus L.***

3. (10 Pts) A hydrogen stream to a fuel cell must be cleaned up of any CO, since CO will poison the catalyst. The removal of CO can be done with a catalyst that combusts CO selectively in the presence of H_2. The kinetics for the two reactions are given by:

1. $CO + 1/2O_2 \rightarrow CO_2$	$r_1 = k_1P_{O2}/P_{CO}$	$k_1 = k_1^o\exp(-E_1/RT)$
2. $H_2 + 1/2O_2 \rightarrow H_2O$	$r_2 = k_2P_{O2}P_{H2}$	$k_2 = k_2^o\exp(-E_2/RT)$

$E_1 > E_2$

a) What type of reactor should be used to maximize the combustion of CO relative to H_2? Please be sure to explain your answer.

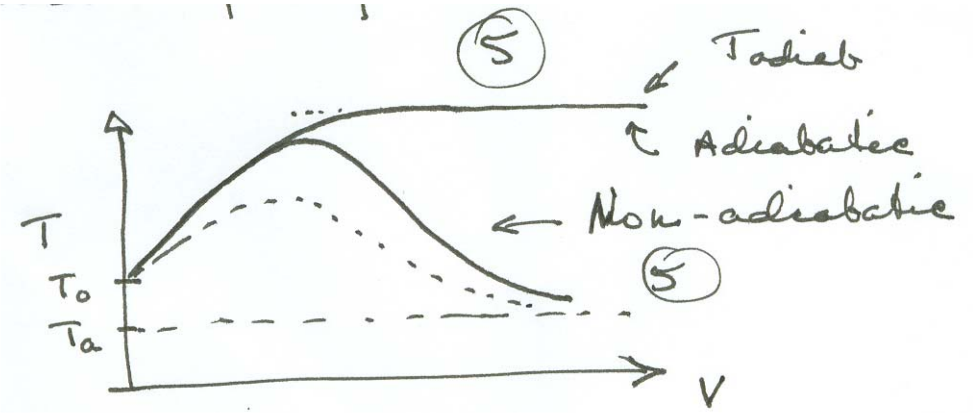
One should use a CSTR in order to maximize the combustion of CO relative to H_2***. The reason is that the rate of CO Combustion is inversely dependent on CO partial pressure, whereas the combustion of*** H_2 ***is proportional to*** H_2 ***partial pressure.***

b) Should the reactor of your choice be run at high or low temperature? Be sure to explain your answer.

The reaction should be run at high T because $E_1 > E_2$; therefore, the rate of reaction 1 will increase more rapidly as T is increased

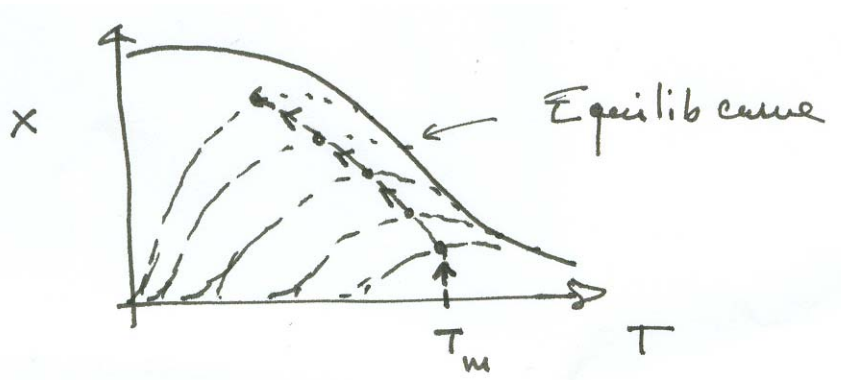
4. (20 Pts.) Consider a first-order gas-phase reaction occurring in a PFR. The reactor is jacketed so that heat can be added or removed through the walls of the reactor. The heat flux through the wall per unit volume of reactor is given by $q = Ua(Ta-T)$.

   a) Assume the reaction is exothermic and reversible. On the same graph, sketch the temperature profile (T versus V) for the following two cases: 1) adiabatic operation, 2) non-adiabatic operation and $T_a < T_o$. Label T_a and T_o on your graph.



T for adiabatic operation will start at To, increase for some distance into the reactor and then level off. For non-adiabatic operation (Ta < To), the T profile will increase initially, then as the reaction slows, heat removal begins to dominate and the temperature is shifted to lower temperatures.

   b) On a separate graph, sketch the optimal temperature profile to maximize the conversion. Assume the maximum operating temperature is T_m.



For part b, the reactor should initially be run at Tm, the maximum possible temperature, until the conversion reaches the "locus of maximum rates." The optimal temperature profile will then decrease along this locus.

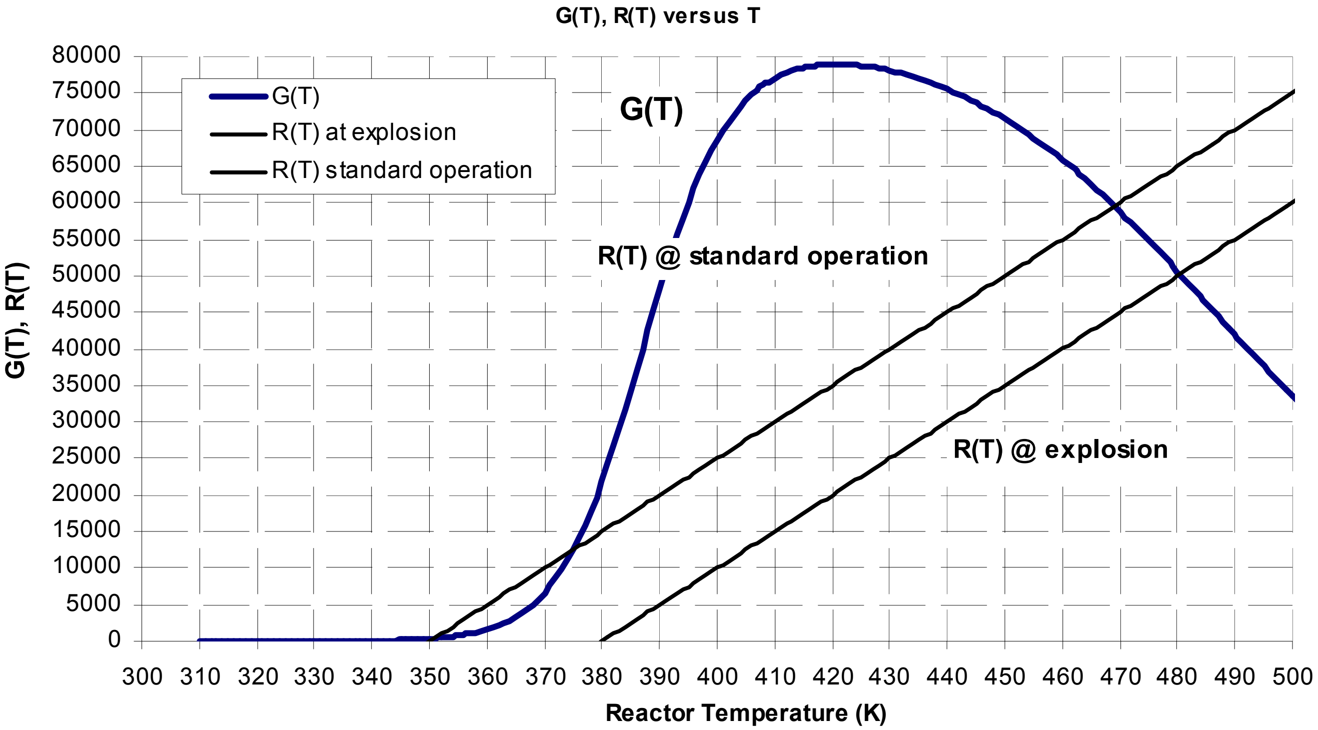
5. (30 Pts.) The liquid phase reaction of $J \leftrightarrow Z$ takes place in a superheated steam jacketed CSTR with pure J as the feed. An operator in charge of monitoring the reactor decides that everything is quiet and steps out to have a quick cup of coffee. While away, a loud explosion is heard coming from the direction of the CSTR. The operator runs back and finds that the CSTR has exploded. In the follow-up investigation, the reactor was found to have heated up to above the reactor design specifications. The shaken operator explained that the reactor was definitely operating below 370 K when she left.

The last readings on operator's clipboard:

Inlet feed temperature = 305K
Temperature of the heated jacket = 355K
Molar flowrate of feed = 10 mol/min

Reactor Specifications:

$E/R = 20{,}000$ K
$C_{pJ} = 50$ cal/mol·K
$C_{pZ} = 20$ cal/mol·K
$U \cdot A = 4500$ cal/min·K
$\Delta H_{rxn} = -83{,}000$ cal/mol·K
volumetric flowrate = 20 dm^3/min



a) Approximately what was the temperature of the reactor when the operator left for coffee? Use plot shown above.

$$\kappa = \frac{UA}{\sum \Theta_i \tilde{C}_{pi} F_{J0}} = \frac{4500 cal/\min - K}{(50 cal/mol - K) * (10 mol/\min)} = 9$$

$$T_c = \frac{\kappa T_a + T_0}{1+\kappa} = \frac{(9 * 355K) + 305K}{1+9} = 350K$$

$$R(T) = \sum \Theta_i \tilde{C}_{pi} (1+\kappa)(T - T_c) = (50 cal/mol - K)(1+9)(T - 350K) = 500 cal/mol - K (T - 350K)$$

T ≈ 350 K because problem statement said T < 370K when operator left.

b) Could the reactor operate at another temperature(s) under the conditions when the operator left? If so, at what temperature(s)? Show work.

Yes. Steady States at T ≈ 350 K, ≈ 375 K, & ≈ 469 K.
See plot for intercept points of G(T) & R(T)

c) Which temperature(s) are most likely to occur? (i.e., stable)

Stable Steady States at T ≈ 350 K & ≈ 469 K. Unstable at T ≈ 375 K

d) The investigators found that the control mechanism for the superheated steam jacket was jammed open and the final reactor temperature (assumed at steady state) before the CSTR exploded was 480K. What was the temperature of the heated jacket when the reactor exploded? Show calculation.

Looking at graph: R(T=480K) = 50,000

Kappa and heat capacity are constant so then:

$$50{,}000 = R(T) = (50 cal/mol - K)(1+9)(480K - T_c) = 500 cal/mol - K (480K - T_c)$$

Tc = 380K
then:

$$380K = T_c = \frac{\kappa T_a + T_0}{1+\kappa} = \frac{(9 * T_a) + 305K}{1+9}$$

Ta = 388.3 K

e) What was the conversion right before the reaction exploded?

$$G(T) = (-\Delta H_{rxn}) X$$

Looking at plot: G(T) = 50,000; therefore, X = 0.602