Chemical & Biomolecular Engineering 142

Chemical Kinetics and Reaction Engineering

Midterm 2

Thursday, November 3, 2011

The exam is 100 points total and 20% of the course grade. Please read through the questions very carefully before answering. Make sure to show all your work. Good luck !

Name ____

Student ID____

Problems	Points (Max.)	Points Received
1	40	
2	44	
3	16	

You are allowed one 8.5”’x 11” sheet of paper and a calculator for this exam. A list of (possibly) useful integrals is provided on the last page of this exam.

Problem 1

Consider a non-isothermal liquid-phase batch reactor initially charged with inert solvent and reagent A, which reacts according to zero-order kinetics to yield product B in the exothermic reaction A → B. Please make sure to read all parts of this question, and clearly show your reasoning. Answers without justification/reasoning automatically receive no credit.

Additional Information:

Zero-order rate constant k (mol/m^3 s)
$k = C_1 + C_2 T$, where C1 and C2 are constants independent of T (T = reactor temperature (K))
(Note: Instead of the usual Arrhenius expression involving exponentials, the k above has been linearized in the temperature window of interest using a Taylor series expansion)

U = overall heat transfer coefficient (W/m^2 K)

A = heat transfer area available in reactor (m^2)

T_{am} = ambient temperature (K)

ΔH^0_{rxn} = standard-state enthalpy change of reaction per mole of A reacted < 0

V = reactor volume

C_P = same molar heat capacity for all species in reactor including inert solvent (J/mol K)

N_{A0} = initial amount of A charged to reactor (moles)

N_S = amount of inert solvent charged to reactor (moles)

T_0 = reactor temperature at t=0

(a) Derive an analytical expression for the reactor temperature T as a function of time t before reactant A is completely depleted in the reactor. (10 points)

Energy Balance:

For a batch reactor.

$$\dot{Q} = \frac{dH}{dt}.$$

$$UA(T_A - T) = -\frac{dN_A}{dt}\Delta H^\circ_{Rxn} + N_{T0} C_p \frac{dT}{dt}.$$

$$\frac{dT}{dt} = \frac{UA(T_A - T) + \frac{dN_A}{dt}\Delta H^\circ_{Rxn}}{(\underbrace{N_A + N_B + N_S}_{N_{T0}})C_p} \qquad \boxed{(+2 \text{ pts})}$$

Mole Balance:

$$r_A V = \frac{dN_A}{dt}.$$

$$-kV = \frac{dN_A}{dt}.$$

$$-(C_1 + C_2 T)V = \frac{dN_A}{dt}. \qquad \boxed{(+2 \text{ pts}).}$$

Plug in:

$$\frac{dT}{dt} = \frac{UA(T_A - T) - \Delta H^\circ_{Rxn}(C_1 + C_2 T)V}{(N_{A0} + N_S)C_p}. \qquad \boxed{(+1 \text{ pt})}$$

$$\frac{dT}{dt} = \underbrace{\frac{UA\,T_A - \Delta H^\circ_{Rxn} C_1 V}{(N_{A0} + N_S)C_p}}_{\alpha.} - \underbrace{\frac{UA + C_2 V \Delta H^\circ_{Rxn}}{(N_{A0} + N_S)C_p}}_{\beta.} T.$$

$$\frac{dT}{dt} = \alpha - \beta T$$

$$\frac{dT}{\alpha - \beta T} = dt.$$

+1 $$-\frac{1}{\beta}\log(\alpha - \beta T)\Big|_{T_0}^{T(t)} = t$$

$\boxed{(+2 \text{ pts})}$ $$\log\frac{\alpha - \beta T(t)}{\alpha - \beta T_0} = -\beta t.$$

$$\alpha - \beta T(t) = (\alpha - \beta T_0)\exp -\beta t.$$

$$T(t) = \frac{\alpha - (\alpha - \beta T_0)\exp -\beta t}{\beta}.$$

$$T(t) = \left.\frac{UA\,T_A - \Delta H^\circ_{Rxn} C_1 V}{UA + C_2 V \Delta H^\circ_{Rxn}}\right\} \boxed{+1 \text{ pt}}$$

$$-\underbrace{\frac{UA(T_A - T_0) - \Delta H^\circ_{Rxn} V (C_1 + C_2 T_0)}{UA + C_2 V \Delta H^\circ_{Rxn}}}_{\boxed{+1 \text{ pt}}} \exp - \underbrace{\frac{UA + C_2 V \Delta H}{(N_{A0} + N_S)C}}_{\boxed{+1 \text{ pt}}}$$

(b) Derive an expression to find out the time it take to deplete all reactant A in the reactor. Your expression should consist of an implicit equation for time of the form f(t) =Y, where f(t) is some function of t. (15 points)

$$\frac{dN_A}{dt} = -(C_1 + C_2 T) V \qquad \boxed{(+2pt)}$$

$$\int dN_A = -\int (C_1 + C_2 T)\, V\, dt.$$

$$N_{A0} - 0 = -\int_{t_{max}}^{0} (C_1 + C_2 T) V \cdot dt$$

$$N_{A0} = \int_{0}^{t_{max}} (C_1 + C_2 T) V\, dt \qquad \boxed{(+2\,pt)}$$

let $T(t)$ be abbreviated as.

$$T(t) = \gamma - \xi \exp -\phi t.$$

$$N_{A0} = V \int [C_1 + C_2(\gamma - \xi \exp - \phi t)]\, dt. \qquad \text{substitute in } \boxed{(+2pt)}$$

$$C_{A0} = C_1 t + C_2 \gamma t + \frac{C_2 \xi}{\phi} \exp -\phi t \Big|_{0}^{t_{max}} \qquad \text{correct integration } \boxed{(+3pt)} \quad \text{correct bounds } \boxed{(+2pt)}$$

$$= (C_1 + C_2 \gamma)\, t_{max} + \frac{C_2 \xi}{\phi}\left[\exp(-\phi t_{max}) - 1\right] \qquad \boxed{(+2pt)}$$

$$= \left(C_1 + C_2 \frac{UA\,T_a - \Delta H^\circ_{rxn} C_1 V}{UA + C_2 V \Delta H^\circ_{rxn}}\right) t_{max} + C_2 \frac{UA(T_A - T_0) - \Delta H^\circ_{rxn} V (C_1 + C_2 T_0)}{(UA + C_2 V \Delta H^\circ_{rxn})^2} (N_{A0} + N_S) C_p$$

$$\times \left[\exp\left(-\frac{UA + C_2 V \Delta H^\circ_{rxn}}{(N_{A0} + N_S) C_p} t_{max}\right) - 1\right]$$

$$\boxed{(+2\,pt)}$$

(c) After a certain time, all reactant A will be depleted. Derive an analytical expression for the reactor temperature T as a function of time t after reactant A has been depleted in the reactor. (10 points)

After the reaction has gone to completion.

$$UA(T_A - T) = (N_{A0} + N_S)C_p \frac{dT}{dt}$$ $\boxed{(+3\ pt)}$

$$\frac{UA}{(N_{A0}+N_S)C_p}\,dt = \frac{dT}{T_A - T}$$

$$\frac{UA}{(N_{A0}+N_S)C_p}\,t = -\log\frac{T_A - T}{T_A - T_{max}}$$ where $T_{max} = T(t_{max})$ $\boxed{(+3\ pt)}$

(from last problem.
→ Definition $\boxed{(+1\ pt)}$

$$\frac{T_A - T}{T_A - T_{max}} = \exp -\frac{UA}{(N_{A0}+N_S)C_p}\,t$$

$$T = T_A - (T_A - T_{max})\exp -\frac{UA}{(N_{A0}+N_S)C_p}\,t$$ $\boxed{(+3\ pt)}$

(d) What will the final temperature of the reactor be after a very long, infinite time? (5 points)

Take the expression from part (c)

$$\lim_{t\to\infty} T(t) = T_A - (T_A - T_{max})\underbrace{\exp -\frac{UA}{(N_{A0}+N_S)C_p}\,t}_{\to 0}$$

$$= T_A$$

+3 pts for taking the limit

+2 pts for answer.

Problem 2

The elementary, exothermic, irreversible gas-phase reaction A → B + C (rate constant k) is carried out in an adiabatic reactor under steady state conditions. Species A and an inert I are fed to the reactor in equimolar amounts at temperature T_0. Species A, B and C all have the same heat capacity equal to C_P. And T_{max} is the maximum temperature that can be sustained by the reactor.

Additional Information:

C_P (molar heat capacity of A, B and C) = 30 J mol^{-1} K^{-1}
$C_{P,I}$ (molar heat capacity of Inert, I) = 5 J mol^{-1} K^{-1}
F_{T0} (total molar flow rate of the feed) = 40 mol min^{-1}
T_0 (feed temperature) = 500 K
T_{max} (maximum temperature sustained by the reactor) = 1000 K
ΔH^{o}_{rxn} (300 K) (standard heat of reaction) = - 800 J mol^{-1}
k(T) (first order rate constant) = 0.02 + 0.01(T-300) min^{-1}
v_0 (initial volumetric flow rate of the feed) = 10 dm^3/min

(a) In words, describe what two enthalpies have to be equal to each other in any adiabatic reactor. (5 points)

∵ Adiabatic reactor

⇒ No communication of heat with surroundings
(All energy would remain in reactor)

⇒ Enthalpy change to change feed temp to reactor temperature = Enthalpy Change due to heat of reaction

$$\underbrace{F_{A0}\sum \Theta_i C_{pi} (T-T_0)} = \underbrace{-(-\Delta H_{rxn}) F_{A0} X_A}$$

5pt

(b) Given the constraints above, find the maximum conversion that can be achieved in the reactor. Write all the assumptions made and explanation of why you made those assumptions in few words. (10 points)

$A \longrightarrow B + C$

Energy Balance :-

$$\cancel{\dot{Q}} - \cancel{\dot{W}_s} + \sum F_{i0} H_{i0} - \sum F_i H_i = \cancel{\frac{dE_{sys}}{dt}}$$

(1 Pt) $= 0$ (Adiabatic reactor)

$(= 0$ (1pt) negligible)

$(= 0$, (1Pt) Steady state)

So,

$$\sum F_{i0} H_{i0} = \sum F_i H_i$$

$$F_{A0} H_{A0} + F_{I0} H_{I0} = F_A H_A + F_B H_B + F_C H_C + F_I H_I$$

$$F_{A0} H_{A0} + F_{I0} H_{I0} = F_{A0}(1-X_A) H_A + F_{A0} X_A H_B + F_{A0} X_A H_C + F_{I0} H_I$$

$$F_{A0}(H_{A0} - H_A) + F_{I0}(H_{I0} - H_I) = F_{A0} X_A [\underbrace{H_B + H_C - H_A}_{= \Delta H_{rxn}(T)}]$$

$\because$ $H(T) = H(T_{ref}) + \int C_p \, dT$ (No phase change)

$$\Rightarrow F_{A0}(C_{PA}(T_0 - T)) + (\Theta_I F_{A0})(C_{PI}(T_0 - T)) = F_{A0} X_A [\Delta H_{rxn}(T)]$$

$$\Rightarrow -F_{A0} \sum \Theta_i C_{Pi} (T - T_0) = F_{A0} X_A (\Delta H_{rxn}(T)) \quad \text{(2pt)}$$

$$\Delta H_{rxn}(T) = \Delta H^{\circ}_{rxn}(T_{ref}) + \Delta C_p (T - T_{ref}) \quad \text{(1pt)}$$

$T_{ref} = 300$, $\Delta C_p = C_{PB} + C_{PC} - C_{PA} = C_p + C_p - C_p = C_p$ (1 Pt), $\sum \Theta_i C_{Pi} = C_{PA} + \Theta_I C_{PI}$

$$\Delta H_{rxn}(T) = \Delta H_{rxn}(300K) + C_p(T - 300)$$

$$\Rightarrow \boxed{-F_{A0}(C_{PA} + \Theta_I C_{PI})(T - T_0) = F_{A0} X_A [\Delta H^{\circ}_{rxn}(300K) + C_p(T - 300)]}$$

$$\Rightarrow \quad (C_{pA} + \theta_I C_{pI})(T_0 - T) = X_A\left[\Delta H^{\circ}_{rxn}(300K) + C_p(T-300)\right]$$

when $T = T_{max}, (=1000\,K)$

$$X_{A_{at\,T_{max}}} = \frac{[30 + (1\times5)][500-1000]}{[-800 + 30(1000-300)]} \Rightarrow \frac{-17500}{20300} \Rightarrow -0.8660$$

$X_{A_{at\,T_{max}}} \Rightarrow -0.866$ doesn't make sense.

Check T at $X_{A_{max}} = 1$

$$\Rightarrow \quad (30+5)(500-T) = 1[-800 + 30(T-300)]$$

$$\Rightarrow \quad \boxed{T \Rightarrow 420\,K}$$

$T < T_{max} (=1000\,K)$

thus maximum conversion acheivable is (3pt)

100% conversion. ($\because$ T ↓, thus it would never reach T above 1000 K in reactor.)

(c) If conversion of A achieved in the reactor is 80 %, what is the temperature at the outlet of the reactor? (10 points)

using the same equation as part (b) -

$$\Sigma F_{i0} H_{i0} = \Sigma F_i^\circ H_i^\circ \quad (2\,pt)$$

$$\left(C_{pA} + \theta_I C_{pI}\right)(T_0 - T) = X_A\left[\Delta H^\circ_{rxn}(300K) + C_p\,(T-300)\right]$$

$$\because X_A = 0.8$$

$$\Rightarrow \quad (30+5)(500-T) = 0.8\left[-800 + 30\,(T-300)\right] \quad (4\,pt)$$

$$\Rightarrow \quad \boxed{T = 429.49\ K} \quad (4t)$$

(d) If the reaction in part (c) is actually carried out in an adiabatic (i) CSTR or (ii) PFR, would the temperature for both of these cases at the outlet be lower, higher or same as calculated in part (c)? Why? (1-2 sentences) (4 points)

T would be same in CSTR as well as in PFR. (2pt)

∵ All the Energy is in reactor. Adiabatic balance ~~is~~ just depend on Enthalpies now which is state function. Thus, doesn't depend on reactor type. (2pt)

(e) Consider now that the reaction in part (c) is carried out in an ideal adiabatic CSTR. What should be the volume of the reactor to achieve 80% conversion of A in the reactor? (10 points)

$A \rightarrow B + C$

F_{A0} 0 0

$F_{A0}(1-X_A)$ $F_{A0}X_A$ $F_{A0}X$

$\frac{v}{v_0} = \frac{F_T T}{F_{T0} T_0} = \left(\frac{T}{T_0}\right)\frac{F_{A0}+F_{I0}}{F_{A0}(1+X_A)+}$

(∵ $F_{I0} = F_{A0}$)

$\frac{v}{v_0} = \left(\frac{T}{T_0}\right)\frac{2F_{A0}}{F_{A0}(2+X_A)} \Rightarrow$

(2 Pt

Mol Balance on (A) —

In − Out + Gen = Acc

$$F_{A0} - F_A + (r_A V) = \cancel{\frac{dN_A}{dt}} \; (=0, SS)$$

$$F_{A0} X_A = \underset{(2pt)}{(-r_A V)} = k C_A V = k \frac{F_A}{v} V = \frac{k F_{A0}(1-X_A)}{v_0(1+\frac{X}{2})(T}$$

$$\cancel{F_{A0}} X_A = \frac{k \cancel{F_{A0}} (1-X_A) V}{v_0 (1+\frac{X_A}{2}) (T/T_0)}$$

$$V = \frac{v_0 (1+X_A/2) X_A}{k(1-X_A)}\left(\frac{T}{T_0}\right) \; (3pt) = \frac{10(1+0.4)(0.8)\left(\frac{429.49}{500}\right)}{(0.2)\times[0.02+0.01(429.29-}$$

$\boxed{k = 1.91}$

$$\boxed{V = 36.63 \text{ dm}^3}$$

(3pt)

(f) If a heat exchanger with a coolant stream is added to the reactor system with heat transfer coefficient U and heat transfer area A, how would your mole and energy balance for part (c) and (e) change? Write balance(s) to reflect this change. Do not solve the equations. (5 points)

Mol Balance → No effect (2pt)

Energy Balance →

$$\boxed{\dot{Q}} - \underbrace{\cancel{\dot{W}_s}}_{(=0)} + \sum F_{i0} H_{i0} - \sum F_i H_i = \underbrace{\cancel{\frac{dE_{sys}}{dt}}}_{(=0,\ ss)}$$

↓

$\neq 0$

↳ $\dot{Q} = UA(T_a - T)$

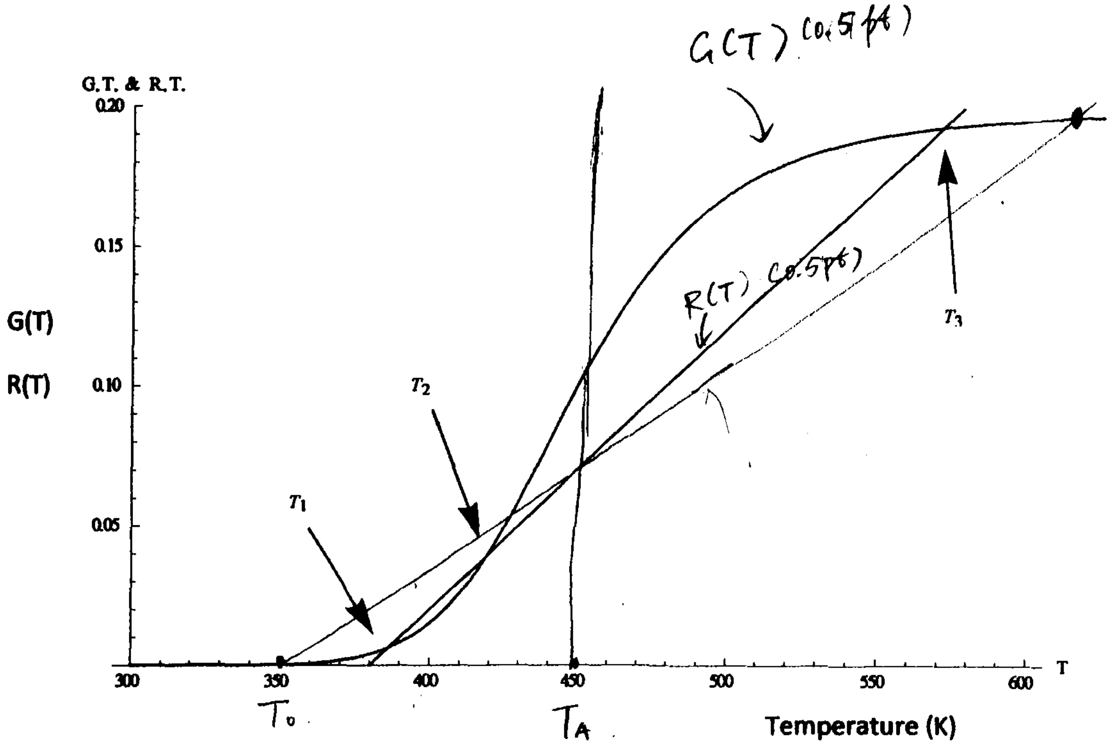
$$\Rightarrow \quad UA(T_a - T) + \sum F_{i0} H_{i0} - \sum F_i H_i = 0$$

or

$$\boxed{UA(T_a - T) + F_{A0} \sum \Theta_i C_{p_i}(T_0 - T) - \Delta H_{rxn}(T) F_{A0} X_A = 0}$$

(3pt)

Problem 3 (2 points each)



(a) Identify G(T) and R(T) on the graph. (label on graph)

According to the G(T) and R(T) plot above, what happens to the CSTR (heats up, cools down, etc.) if it is started up at the following conditions (part (b) – part (g)). For the purposes of this problem, assume perfect control of all imposed temperatures.

Inlet temperature T_0 = 350K, ambient /cooling jacket temperature T_A = 450K.

(b) T= 350K

$G(T) > R(T)$ (1 pt)

Heats up → T_1 (1 pt).

(c) $T = T_2$

$G(T) = R(T)$. (1 pt)

stays constant due to perfect control. (1 pt)

(d) T=400K

$G(T) < R(T)$. (1 pt)

cools down $\rightarrow T_1$ (1 pt)

(e) T=500K

$G(T) > R(T)$ (1 pt)

heats up $\rightarrow T_3$ (1 pt)

(f) T=600K

$G(T) < R(T)$	(1 pt)
cools down → T_3	(1 pt)

(g) It is potentially unsafe to operate your reactor above 550K, what is the range of applicable initial temperatures of the reactor?

$T \leq T_2$.

(1 pt for stating $T < T_2$)

(1 pt for stating $T = T_2$ is also valid).

(h) An accident has happened and caused the cooling jacket to fail. The reactor is now operating adiabatically. Draw the new R(T) and clearly label the operating state of the reactor on the graph.

a verticle line at T_a.	(0.5 pt)
triple intersection	(0.5 pt).
correct $R(T)$	(1 pt).
label steady state	(1 pt)