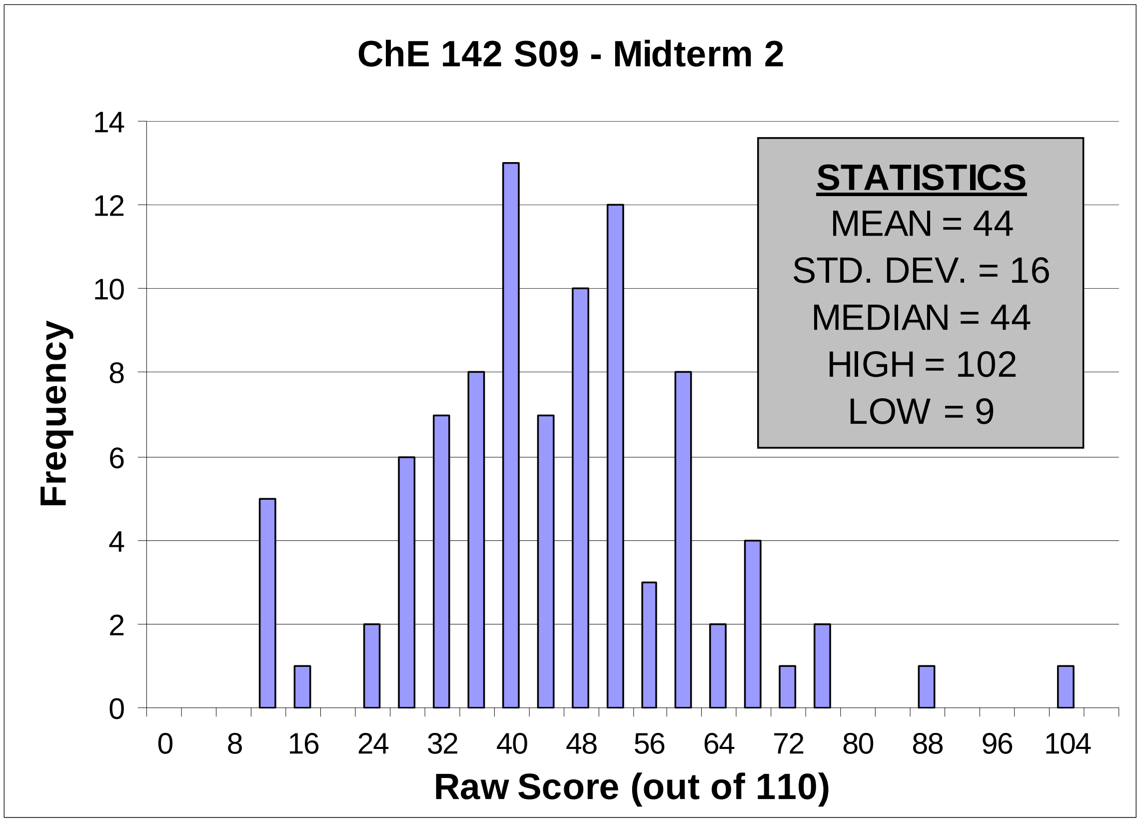
Chemical Kinetics and Reaction Engineering

ChE 142 – Spring 2009

MIDTERM EXAMINATION II
SOLUTIONS



Problem 1a

(i) The inert packing causes a pressure drop along the reactor. According to LeChatelier's principle, a decrease in pressure will shift equilibrium to the right ($\delta > 0$) and <u>increase</u> the equilibrium conversion.

Alternatively, this can be shown mathematically:

$$K_P = e^{-\Delta G^\circ/RT} = e^{\Delta S^\circ/R} e^{-\Delta H^\circ/RT} = \frac{P_B^{\,2} P_c}{P_A^{\,2}} = P\left(\frac{y_B^{\,2} y_c}{y_A^{\,2}}\right)$$

$$e^{\Delta S^\circ/R} e^{-\Delta H^\circ/RT} = P\left(\frac{y_B^{\,2} y_c}{y_A^{\,2}}\right)$$

If *T* is constant, the value of K_P (left-hand side) is constant. If *P* decreases, then the term containing the ratio of mole fractions must increase to maintain equilibrium, which can only happen if the <u>conversion increases</u> because all of the species are related (through stoichiometry) by the same reaction.

(ii) In an adiabatic reactor, an endothermic reaction will cause the temperature to decrease with increasing conversion. According to LeChatelier's principle, as the temperature decreases, equilibrium will shift to the left (containing the "heat" term) which will <u>decrease</u> the equilibrium conversion.

Alternatively, this can be shown mathematically using the relationship derived in part (a):

$$e^{\Delta S^\circ/R} e^{-\Delta H^\circ/RT} = P\left(\frac{y_B^{\,2} y_c}{y_A^{\,2}}\right)$$

As *T* decreases, the value of K_P (left-hand side) decreases for an endothermic reaction ($\Delta H_R > 0$). If *P* is constant, then the term containing the ratio of mole fractions must decrease to maintain equilibrium, which can only happen if the <u>conversion decreases</u> because all of the species are related (through stoichiometry) by the same reaction.

Problem 1b

The long-chain approximation is valid for any reaction propagated via radicals and assumes that the rate of any propagation step is much faster than the rate of any initiation or termination step ($r_p >> r_i, r_t$).

This is a reasonable assumption to make because initiation steps are rare events with high activation energies that result from needing to a stable bond to form two unstable radical species, while propagation steps are essentially unactivated processes in which the radical is transferred from one species to another.

In deriving rate equations, the LCA allows PSSH equations written for the concentration of any radical species to account for only the changes due to propagation steps. This assumption on the propagation steps sets the identity that

$$\frac{d\left(R\bullet\right)}{dt} = r_i - r_t \approx 0$$

at pseudo-steady-state, where (R●) is the total radical concentration.

Problem 1c

(i) For an adiabatic reactor, R(T) reduces to:

$$R\left(T\right) = \overline{C_{P0}}\left(T - T_0\right)$$
$$\overline{C_{P0}} = \theta_A C_{PA} + \theta_B C_{PB} = \left(1\right)\left(7\right) + \left(1\right)\left(3\right) = 10 \text{ J/mol-K}$$

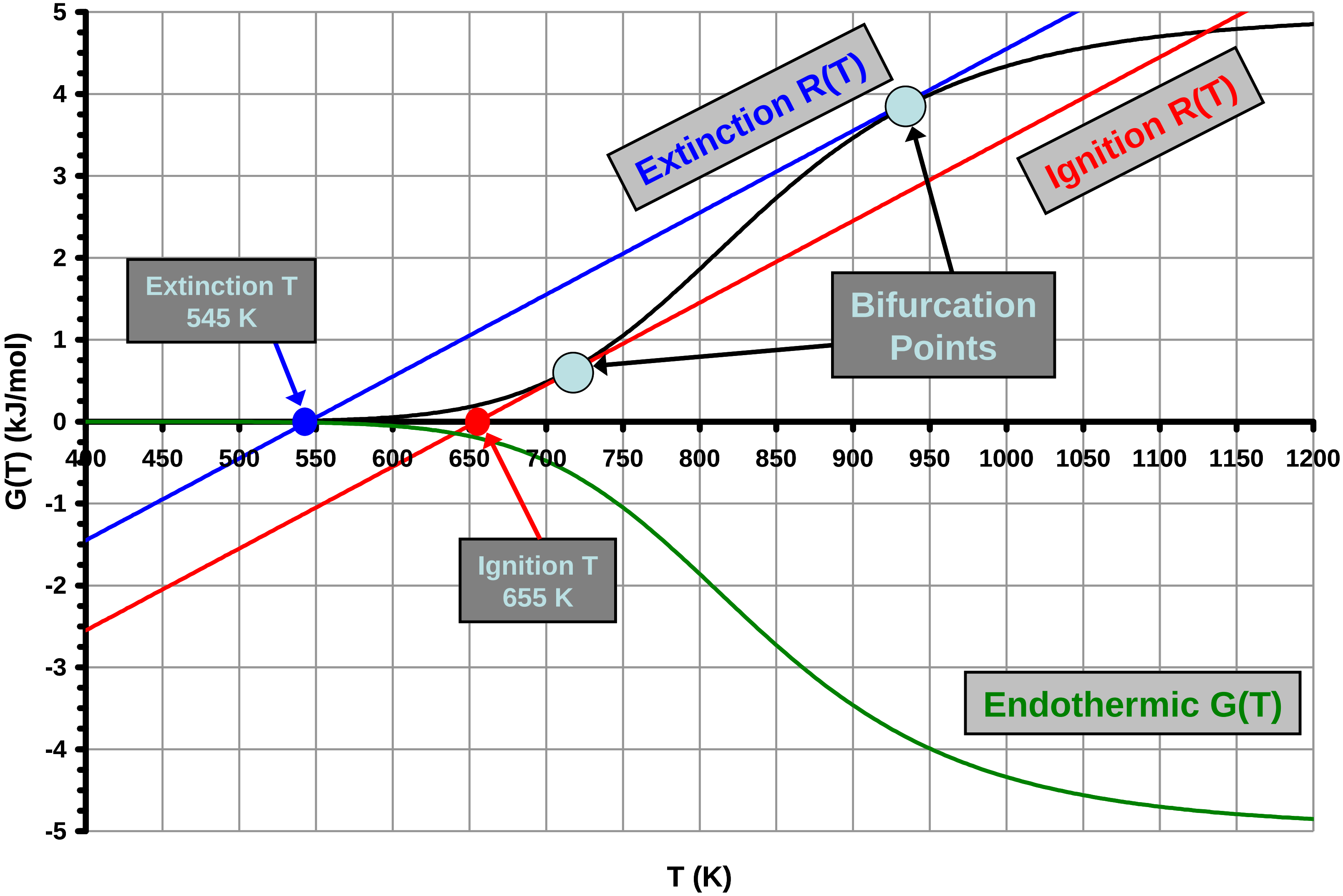
The extinction and ignition R(T) curves have slopes of 0.01 kJ/mol-K and are tangent to the G(T) curve (see the attached plot). Their x-intercepts are equal to T_0 and respectively correspond to the extinction (545 K) and ignition (655 K) temperatures.

(ii) $G(T) = X * (-\Delta H_R)$. For an endothermic reaction, G(T) will always be negative and will decrease monotonically with conversion and temperature. Multiple steady-states are not possible for endothermic reactions, because the slope of any R(T) curve is positive and always greater than the maximum slope for an endothermic G(T) curve:

$$\overline{C_{P0}}\left(1+\alpha\right) > \max\left(\frac{\partial G(T)}{\partial T}\right)$$

Therefore, G(T) and R(T) will always intersect in one point that determines the steady-state operating conditions for the reactor.

(iii) When the cooling is turned on, $\alpha > 0$, causing the slope and x-intercept (T^*) of the extinction R(T) to increase. When $T_a = T_0$, $T^* = T_0$; therefore, the extinction temperature <u>increases</u>. (Indeed, using the numbers given in the problem statement, the new extinction temperature can be estimated from the plot to be 610 K).


Extinction R(T)
Ignition R(T)
Bifurcation Points
Extinction T 545 K
Ignition T 655 K
Endothermic G(T)
G(T) (kJ/mol)
T (K)
5
4
3
2
1
0
-1
-2
-3
-4
-5
400
450
500
550
600
650
700
750
800
850
900
950
1000
1050
1100
1150
1200

Problem 2a

Mole Balance:

$$V_1 = \frac{F_{A0,1}x_{A,1}}{-r_{A,1}} = \frac{F_{A0,1}x_{A,1}}{k_1 C_{A0,1}\left(1-x_{A,1}\right)}$$

$$\frac{V_1 k_1 C_{A0,1}}{F_{A0,1}} = k_1\tau_1 = \frac{x_{A,1}}{1-x_{A,1}}$$

$$x_{A,1} = \frac{k_1\tau_1}{1+k_1\tau_1} = \frac{0.5*2}{1+0.5*2} = 0.5$$

Problem 2b

Overall Energy Balance:

$$\frac{dE}{dt} = \dot{Q} - \dot{W}_s - F_{A0,1}\left(\sum_i \theta_i C_{pi}\right)\left(T_1 - T_1\right) - F_{C0,2}\left(\sum_i \theta_i C_{pi}\right)\left(T_1 - T_{0,2}\right) - F_{A0,1}x_{A,1}\Delta H^0_{R1} - F_{C0,2}x_{C,2}\Delta H^0_{R2}$$

Assumptions: Steady-state, no shaft work, adiabatic to surroundings, $T_1 = T_{0,2}$

$$0 = -F_{A0,1}x_{A,1}\Delta H^0_{R1} - F_{C0,2}x_{C,2}\Delta H^0_{R2}$$

Mole Balance:

$$x_C = \frac{k_2\tau}{1+k_2\tau} = \frac{k_2\dfrac{V_2 C_{C0}}{F_{C0}}}{1+k_2\dfrac{V_2 C_{C0}}{F_{C0}}}$$

Substitute mole balance into energy balance

$$\frac{k_2 V_2 C_{C0,2}}{1+k_2\dfrac{V_2 C_{C0,2}}{F_{C0,2}}}\Delta H^0_{R2} = -F_{A0,1}x_{A,1}\Delta H^0_{R1}$$

$$F_{C0,2} = \frac{-k_2 V_2 C_{C0,2}}{\dfrac{k_2 V_2 C_{C0,2}\Delta H^0_{R2}}{F_{A0,1}x_{A,1}\Delta H^0_{R1}} + 1}$$

$$F_{C0,2} = \frac{-\left(1/\min\right)\left(100L\right)\left(5mol/L\right)}{\dfrac{\left(1/\min\right)\left(100L\right)\left(5mol/L\right)\left(25{,}000J/mol\right)}{\left(100mol/\min\right)\left(0.5\right)\left(-50{,}000J/mol\right)} + 1} = 125mol/\min$$

Problem 2c

Energy balance with assumptions: Steady-state, no shaft work, adiabatic to surroundings

$$0 = -F_{C0,2}\left(C_p\right)\left(T_1 - T_{0,2}\right) - F_{A0,1}x_{A,1}\Delta H^0_{R1} - F_{C0,2}x_{C,2}\Delta H^0_{R2}$$

$$0 = -F_{C0,2}\left(C_p\right)\left(T_1 - T_{0,2}\right) - F_{A0,1}x_{A,1}\Delta H^0_{R1} - F_{C0,2}\left(\frac{k_2\dfrac{V_2 C_{C0}}{F_{C0}}}{1 + k_2\dfrac{V_2 C_{C0}}{F_{C0}}}\right)\Delta H^0_{R2}$$

The rate of heat generated by the exothermic reaction in CSTR 1 is constant. Decreasing the inlet temperature to CSTR 2 requires that part of the heat generated from CSTR 1 is used to heat the feed to T_1. As a result, less heat will need to be consumed by the endothermic reaction in CSTR 2, which will occur when the product of F_{C0} and x_c decreases. This product is:

$$F_{C0,2}x_{C,2} = \frac{k_2 V_2 C_{C0}}{1 + \dfrac{k_2 V_2 C_{C0}}{F_{C0}}}$$

F_{C0} must <u>decrease</u> in order for the product of F_{C0} and $X_{C,2}$ to decrease.

Problem 3

a) $r_B = r_2 = k_2(A*)$ ①

QE Step 1 $\quad K_1 = \frac{(A*)^2}{(A_2)(*)^2} \qquad (A*) = \sqrt{K_1(A_2)}\,(*)$

Site balance $\quad [L] = [*) + (A*) + (B*)$ ②

PSSH on B* → not QE

$$r_f = k_2(A*) + k_{-3}(B)(*) - k_3(B*) = 0$$

$$\frac{\left(k_2\sqrt{K_1(A_2)} + k_{-3}(B)\right)(*)}{k_3} = (B*)$$

Substitute into ②.

$$(L) = (*)\left[1 + \sqrt{K_1(A_2)} + \left(\frac{k_2\sqrt{K_1(A_2)} + k_{-3}(B)}{k_3}\right)\right]$$

solve for (*) and substitute into

$$r_B = r_2 = k_2\sqrt{K_1(A_2)}\,(*)$$

$$= \frac{k_2\sqrt{K_1(A_2)}\,(L)}{\left[\underset{\underset{(*)}{\sim}}{1} + \underset{\underset{(A*)}{\sim}}{\sqrt{K_1(A_2)}} + \underset{\underset{(B*)}{\sim}}{\left(\frac{k_2\sqrt{K_1(A_2)} + k_{-3}(B)}{k_3}\right)}\right]}$$

b) when step 3 is QE

$$K_3 = \frac{(B)(*)}{(B*)} \quad \bullet \quad (B*) = \frac{(B)}{K_3}\cdot(*)$$

or $\quad k_{-3}(B\cancel{*}) >> k_2(A*) = k_2\sqrt{K_1(A_2)}\,\cancel{(*)}$

when $(A*), (B*) >> 1$ the second two terms in denominator are much larger than unity

so ...

$$r_B = \frac{k_2 \sqrt{\underline{K}_1 (A_2)}\ (L)}{\left(\sqrt{\underline{K}_1 (A_2)} + (B)/\underline{K}_3\right)}$$

c) $r_c = k_4 (A*) \cdot \frac{(A*)}{(L)}.$

$$= \frac{k_4 \underline{K}_1 (A_2)\ (*)^2}{(L)} = \frac{k_4 \underline{K}_1 (A_2)(L)}{\left(\sqrt{\underline{K}_1 (A_2)} + (B)/\underline{K}_3\right)^2}$$

$$S = \frac{r_B}{r_c} = \left(\frac{k_2}{k_4}\right) \cdot \frac{\left(\sqrt{\underline{K}_1 (A_2)} + (B)/\underline{K}_3\right)}{\sqrt{\underline{K}_1 (A)}}$$

$$= \frac{k_2}{k_4}\left[1 + \frac{(B)}{\underline{K}_3 \sqrt{\underline{K}_1 (A)}}\right]$$

- recycle would increase average (B) and decrease average (A), leading to higher selectivity
- $\frac{k_2}{k_4}$ ↑ as T ↑ so adiabatic conditions give higher T and increase S

  $\underline{K}_3$ and $\underline{K}_1$ ↓ as T increases and higher T also increase the $\frac{(B)}{\underline{K}_3 \sqrt{\underline{K}_1 (A_2)}}$ term.
- (B) helps because it decreases. (A*) and step 2 (to give c) is first order in (A*) while step 4 (to give D) is second order in (A*)