ChE 344
Reaction Engineering and Design

Lecture 14: Thursday, Feb 24, 2022

Non-isothermal reactor design

Reading for today’s Lecture: Chapter 11

Reading for Lecture 15 (Mar 8): Chapter 11, 12

Lecture 14: Non-isothermal Reactor Design
Related Text: Chapter 11.1-11.4

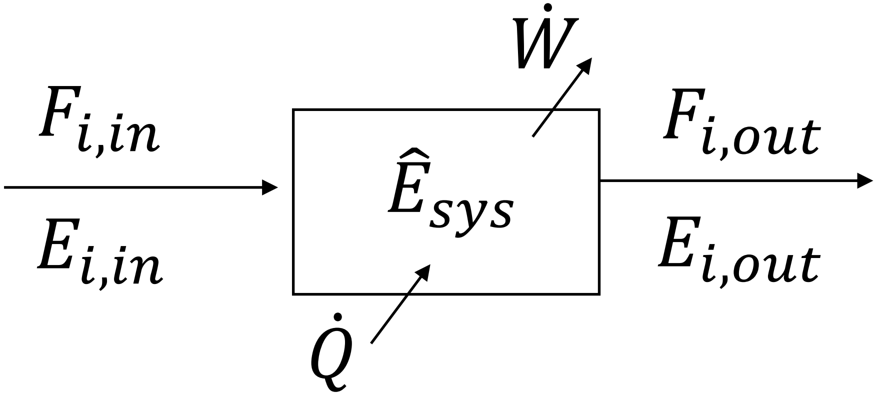
Non-isothermal Algorithm:

Start with normal algorithm used for isothermal reactors:

0. Assumptions
1. Mole Balance: Reactor design equation for the selected reactors
2. Rate Law: To get reaction rate as a function of rate constant, equilibrium constant (for reversible reactions), and concentrations or pressures
    - K_C(T), k(T)
3. Stoichiometry: Consider gas or liquid phase species.
4. Combine: Parts 1-3
    - If needed, may have to include Ergun equation
5. **Solve with energy balance to relate T and X**
6. Evaluate: Use values to get numerical answer

Last time, introduction to non-isothermal reactors, starting with energy balance, then simplifying to get towards adiabatic reactors.

General Energy Balance



We assumed: Negligible potential and kinetic energy, no shear stresses, constant heat capacity with temperature, no phase change from T_{ref}. With some definitions:

$$\sum \nu_i H_i = heat\ of\ reaction\ (at\ outlet\ T) = \Delta H_{rxn}(T_{out})$$

Heat capacities

$$\Delta C_P \equiv \sum \nu_i C_{P,i}$$

ν_A= -1 for lim. reactant A, 0 for inerts

Sum is over all species, but inerts have ν = 0

Discuss with your neighbors:

What is the **heat of reaction** for ammonia synthesis at 150 °C in kcal/mol of N_2 reacted and in kcal/mol H_2 reacted?

$$N_2 + 3H_2 \rightarrow 2NH_3$$

$$H^{\circ}_{NH_3}(25°C) = -11.02\ kcal/mol\ NH_3$$

$$C_{P,NH_3} = 8.92\, cal/mol\ NH_3 \cdot K$$

$$C_{P,N_2} = 6.984\, cal/mol\ N_2 \cdot K$$

$$C_{P,H_2} = 6.992\, cal/mol\ H_2 \cdot K$$

$$H^{\circ}_{H_2}(25°C) = 0$$

$$H^{\circ}_{N_2}(25°C) = 0$$

[✓ A) -23.3 kcal/mol N_2;
-7.766 kcal/mol H_2]

B) -23.3 kcal/mol N_2;
-69.9 kcal/mol H_2

C) -22.04 kcal/mol N_2;
-7.347 kcal/mol H_2

D) -22.04 kcal/mol N_2;
-66.12 kcal/mol H_2

Per mole of nitrogen (as if N_2 is limiting reactant)

$$\Delta H_{rxn}(T = 25°C) = 2H^\circ_{NH_3} - 3H^\circ_{H_2} - H^\circ_{N_2}$$

Per mole of hydrogen (as if H_2 is limiting reactant)

$$\Delta H_{rxn}(T = 25°C) = \frac{2}{3}H^\circ_{NH_3} - 1H^\circ_{H_2} - \frac{1}{3}H^\circ_{N_2}$$

Adjusting to the temperature of interest:

$$\Delta H_{rxn}(150°C) = \Delta H_{rxn}(25°C) + \Delta C_P(150°C - 25°C)$$

Per mole of nitrogen (as if N_2 is limiting reactant)

$$\Delta C_P = 2C_{P,NH_3} - 3C_{P,H_2} - C_{P,N_2}$$

Per mole of hydrogen (as if H_2 is limiting reactant)

$$\Delta C_P = \frac{2}{3}C_{P,NH_3} - 1C_{P,H_2} - \frac{1}{3}C_{P,N_2}$$

Energy balance in terms of heat capacities and heat of reaction with those assumptions/definitions:

(adiabatic only)

$$F_{A0}\left[\left(\sum -\theta_i C_{P,i}[T-T_0]\right) - \left[\Delta H_{rxn}\left(T_{ref}\right) + \Delta C_P\left(T-T_{ref}\right)\right]X\right] + \cancelto{0}{\dot{Q}} - \cancelto{0}{\dot{W}_s} = \cancelto{0}{\frac{d\hat{E}_{sys}}{dt}}$$

$C_{P,i}$ includes all species in the reactor including inerts, but ν_{inert}= zero, so inerts are not included in ΔC_P

Adiabatic reactor (additional assumptions)

1. $\dot{Q} = 0$

2. $\dot{W}_{shaft} = 0$

3. Steady state: $\frac{d\hat{E}_{sys}}{dt} = 0$

$$\left(\sum -\theta_i C_{P,i}[T - T_0]\right) - \left[\Delta H_{rxn}\left(T_{ref}\right) + \Delta C_P\left(T - T_{ref}\right)\right]X = 0$$

Adiabatic energy balance: (Recall T and X relationship)

$$\underset{\nwarrow}{X} = \frac{\sum \theta_i C_{P,i}[T - T_0]}{-\left[\Delta H_{rxn}\left(T_{ref}\right) + \Delta C_P\left(T - T_{ref}\right)\right]}$$

of lim. reactant A

Remember, we can either:

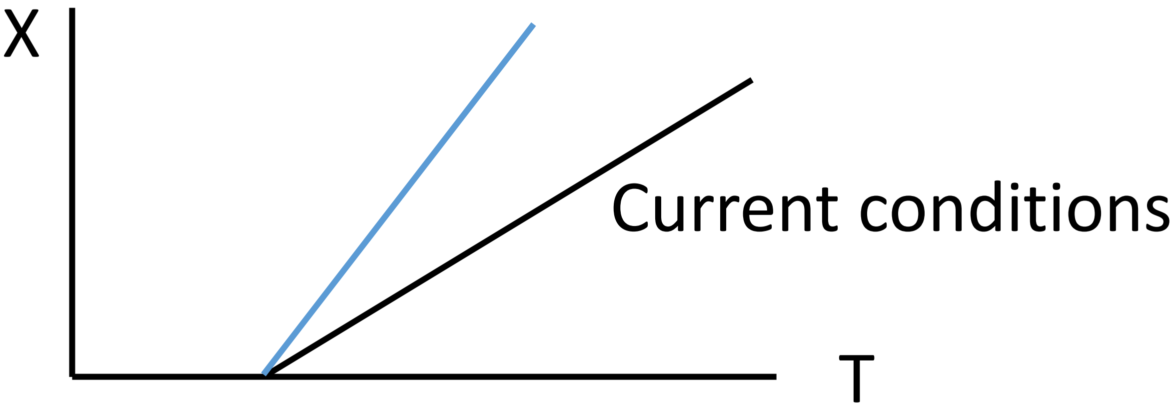
- use this and the rate law to construct a Levenspiel plot,

or

- we can use our normal algorithm of 1) mole balance, 2) rate law, 3) stoichiometry, and then solve using energy balance for T = f(X) with software packages (Polymath, etc.)

Discuss with your neighbors:

If ΔC_P=0, if you increase the flow rate of an inert (water) into your exothermic adiabatic CSTR, what would happen to the slope of X vs. T?



[✓ A) Slope will increase]

B) Slope will decrease

C) Slope will remain the same

D) No way to tell

$$\sum \theta_i C_{P,i}[T - T_0]$$

Includes inerts

Algorithm for solving non-isothermal reactors

PFR (gas-phase):

$$F_{A0}\frac{dX}{dV} = k_f \frac{C_{A0}(1-X)}{1+\varepsilon X}\frac{T_0}{T}\frac{P}{P_0};$$

CSTR:

Rate law, stoich.

$$\frac{F_{A0}-F_A}{-V} = r_A;$$

$$T = f(X)$$

From energy balance

$$k(T) = k(T_1)\exp\left[-\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_1}\right)\right]$$

$$K_C(T) = K_C(T_1)\exp\left[-\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T}-\frac{1}{T_1}\right)\right]$$

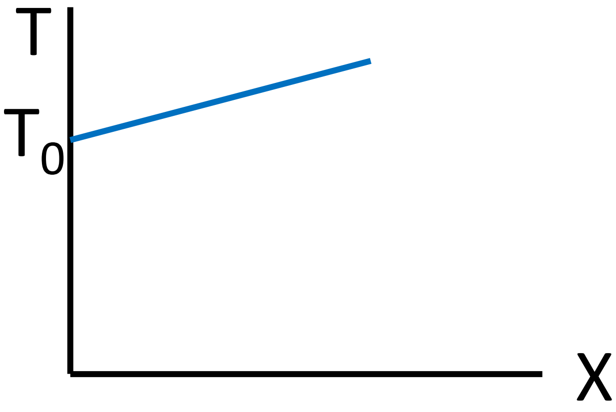
Solve the nonlinear ODE and parameters that depend on T=f(X)

Conceptual Questions: In an adiabatic PFR/batch reactor where A → B, where the reaction is exothermic and $C_{P,A} = C_{P,B}$:

a. Sketch the temperature as a function of conversion

$$X_{EB} = \frac{\sum \theta_i C_{P,i}[T - T_0]}{-\left[\Delta H_{rxn}\left(T_{ref}\right) + \Delta C_P\left(T - T_{ref}\right)\right]}$$

$$X = \frac{C_{P,A}[T - T_0]}{-\left[\Delta H_{rxn}\left(T_{ref}\right) + 0\right]} = \frac{C_{P,A}[T - T_0]}{[+]}$$



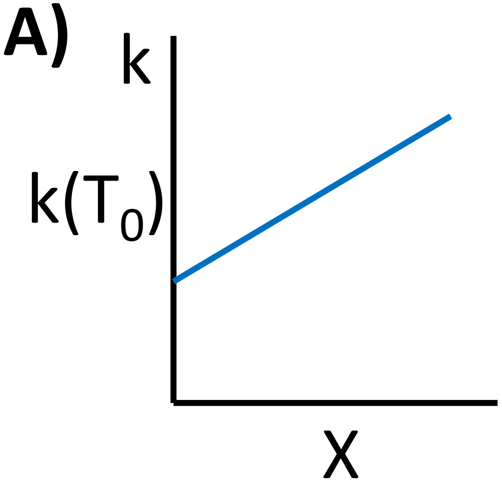
Discuss with your neighbors:

In an adiabatic PFR/batch reactor where A → B, where the reaction is exothermic and $C_{P,A} = C_{P,B}$:

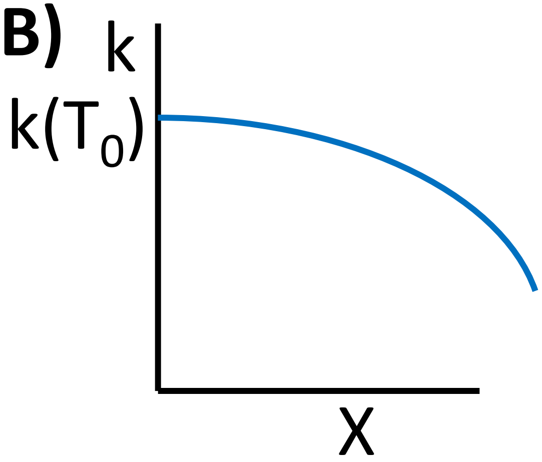
b. Sketch the rate constant as a function of conversion

$$k(T) = k(T_0)\exp\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

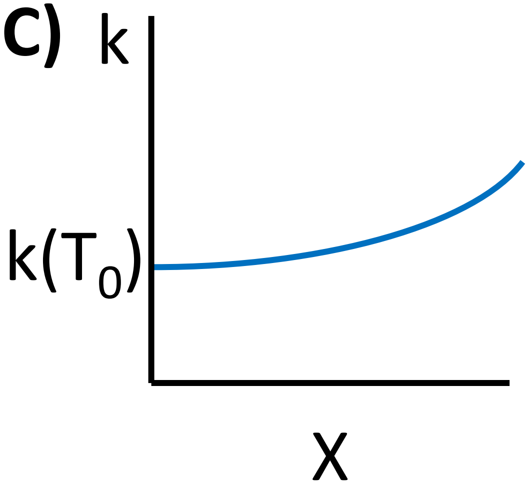
A)



B)



C)



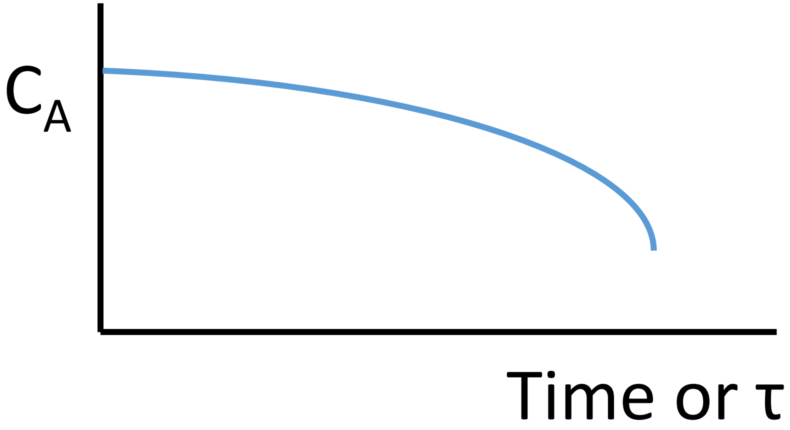
D) Impossible to know if *k* changes

Conceptual Question:

In an adiabatic PFR/batch reactor where A → B, where the reaction is exothermic and $C_{P,A} = C_{P,B}$:

c. Sketch C_A as a function of time or space time, assuming the reaction is zero order in A

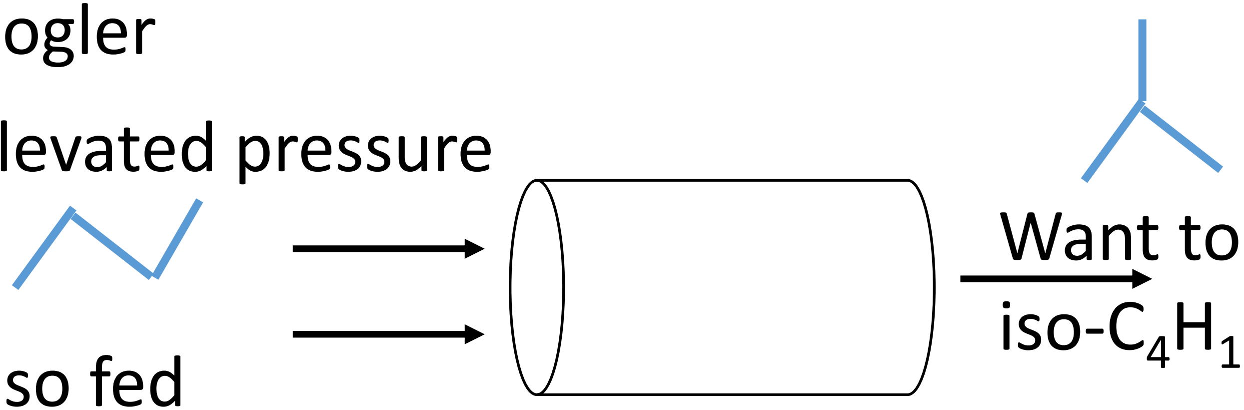
First can recall what happens if C_A is zero order and reaction is isothermal. Now we know that as the reaction proceeds, temperature increases and k increases exponentially, so C_A drops even faster



Example problem: Isomerization of $n\text{-}C_4H_{10}$ (butane)

Example 11-3 Fogler

Liquid phase, elevated pressure



Want to make

$iso\text{-}C_4H_{10}$ B

$n\text{-}C_4H_{10}$ A

$i\text{-}C_5H_{12}$(inert) also fed

F_{T0} = 163 kmol/hr

T_0 = 330 K, but NOT isothermal! Adiabatic reactor

90% nC4, 10% i-C5

$$A \rightleftarrows B$$

$$k_f(360K) = 31.1\ 1/hr$$

ΔH_{rxn} = -6900 J/mol C4, E_a = 65.7 kJ/mol; K_C = 3.03 @ 60 °C;

C_{A0} = 9.3 kmol/m^3

$\overset{A}{C_{P,n\text{-}C4}} = \overset{B}{C_{P,i\text{-}C4}}$ = 141 J/mol·K; $\overset{\text{inert}}{C_{P,i\text{-}C5}}$ = 161 J/mol·K

Question:

1. What is V_{PFR} for $X = 0.5$?

2. What is the Levenspiel plot for this reaction?

Mole balance: PFR design equation

$$F_{A0}\frac{dX}{dV} = -r_A$$

Rate law:

$$r_A = -k_f C_A + k_r C_B = -k_f\left(C_A - \frac{C_B}{K_C}\right)$$

Stoichiometry: Liquid phase

$$C_A = C_{A0}(1 - X);\; C_B = C_{A0}\left(\overset{0}{\theta_B} + \frac{\overset{1}{b}}{\underset{1}{a}}X\right)$$

Combine:

$$F_{A0}\frac{dX}{dV} = -r_A = k_f\left(C_{A0}(1-X) - \frac{C_{A0}X}{K_C}\right)$$

$$\frac{F_{A0}}{k_f\left(C_{A0}(1-X) - \frac{C_{A0}X}{K_C}\right)}dX = dV$$

$$\frac{F_{A0}}{C_{A0}}\frac{1}{k_f\left((1-X) - \frac{X}{K_C}\right)}dX = dV$$

$$\frac{F_{A0}}{C_{A0}}\int_0^X \frac{1}{k_f\left((1-X) - \frac{X}{K_C}\right)}dX = V_{PFR}$$

Evaluate:

$$F_{A0} = 0.9 \times 163\,\frac{kmol}{hr} = 146.7\,\frac{kmol}{hr}$$

$$C_{A0} = 9.3\ kmol/m^3$$

$$15.77 m^3/hr \int_0^X \frac{1}{k_f\left((1-X) - \frac{X}{K_C}\right)} dX = V_{PFR}$$

These are both a function of temperature, which depends on X!

So we will need to incorporate our energy balance equation

Energy balance: Adiabatic reactor

$$F_{A0}\left[\left(\sum -\theta_i C_{P,i}[T-T_0]\right) - \left[\Delta H_{rxn}\left(T_{ref}\right) + \Delta C_P\left(T - T_{ref}\right)\right]X\right] + \cancel{\dot{Q}} - \cancel{\dot{W}_s} = \cancel{\frac{d\hat{E}_{sys}}{dt}}$$

$$\Delta C_P = 0 \; because \; \delta = 0, C_{P,i-C4} = C_{P,n-C4}$$

$$\sum \theta_i C_{P,i} = \theta_A C_{P,n-C4} + \cancelto{0}{\theta_B} C_{P,i-C4} + \theta_{i-C5} C_{P,i-C5}$$

$$\theta_{A=n-C4} = 1$$

$$\theta_{i-C5} = \frac{0.1}{0.9}$$

Inert didn't affect mole balance b/c this was liquid phase, so *v* is constant, but it DOES show up in energy balance!

$$\sum \theta_i C_{P,i} = 141 J/mol \cdot K + \frac{0.1}{0.9} 161 J/mol \cdot K$$

$$= 159\, J/mol \cdot K$$

$$\left[\left(\sum -\theta_i C_{P,i}[T - T_0]\right) - \left[\Delta H_{rxn}(T_{ref})\right]X\right] = 0$$

$$(-159\, J/mol \cdot K[T - 330\, K]) - [-6900\mathrm{J/mol}]X = 0$$

$$-159\, J/mol \cdot K[T - 330\, K] = [-6900\mathrm{J/mol}]X$$

$$[T - 330\, K] = \frac{[-6900\mathrm{J/mol}]X}{-159\, J/mol \cdot K} = (43.4\, K)\, X$$

$$T = (43.4\, K)X + 330\, K$$

Now we have our T = f(X) to combine with mole balance

$$k_f(T) = k_f(360\ K)\exp\left[-\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{360\ K}\right)\right]$$

$$= 31.1\ hr^{-1}\exp\left[-\frac{65700\ J/mol}{8.314\ J/mol\cdot K}\left(\frac{1}{T}-\frac{1}{360\ K}\right)\right]$$

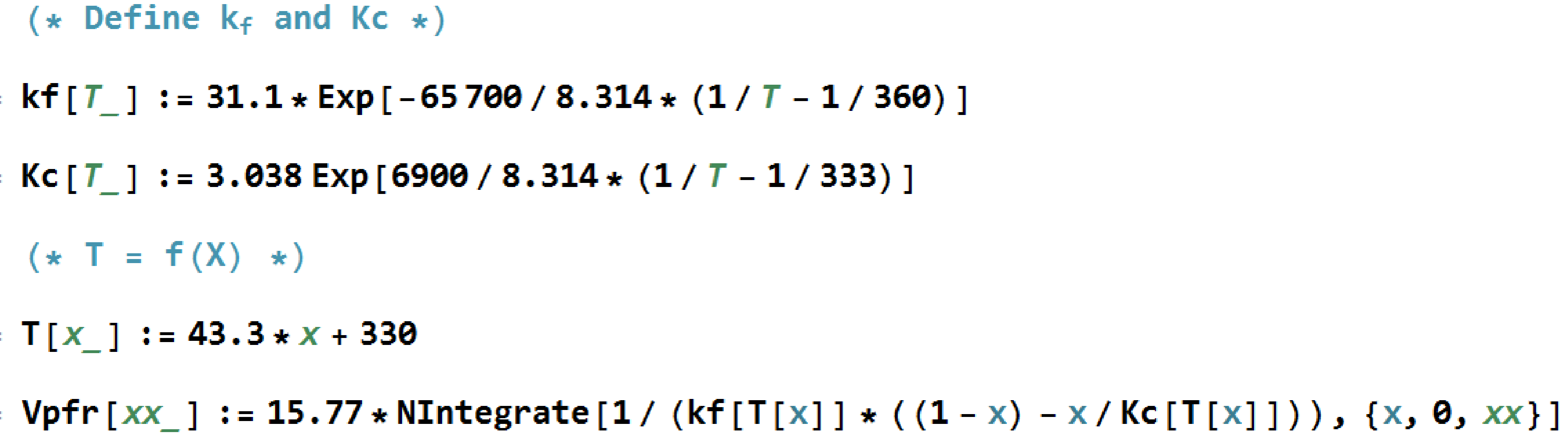
$$K_C(T) = K_C(333\ K)\exp\left[-\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T}-\frac{1}{T_1}\right)\right]$$

$$= 3.03\exp\left[-\frac{-6900\ J/mol}{8.314\ J/mol\cdot K}\left(\frac{1}{T}-\frac{1}{333\ K}\right)\right]$$

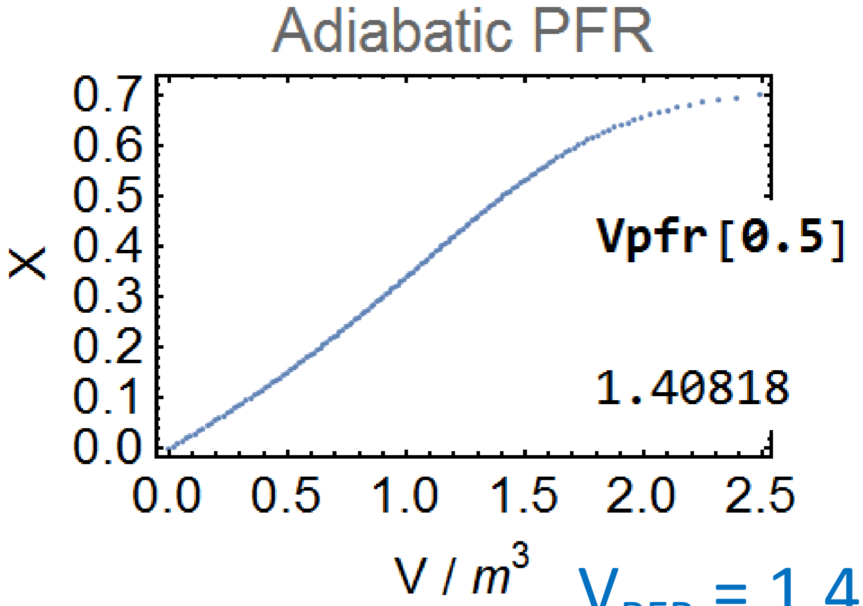
And mole balance from earlier:

$$15.77m^3/hr\int_0^X \frac{1}{k_f\left((1-X)-\frac{X}{K_C}\right)}dX = V_{PFR}$$

Here solving/plotting in Mathematica, but full problem solved on page 563 in book using Polymath (full code on Canvas)



```
(* Define kf and Kc *)

kf[T_] := 31.1 * Exp[-65700 / 8.314 * (1 / T - 1 / 360)]

Kc[T_] := 3.038 Exp[6900 / 8.314 * (1 / T - 1 / 333)]

(* T = f(X) *)

T[x_] := 43.3 * x + 330

Vpfr[xx_] := 15.77 * NIntegrate[1 / (kf[T[x]] * ((1 - x) - x / Kc[T[x]])), {x, 0, xx}]
```



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Vpfr[0.5]

1.40818
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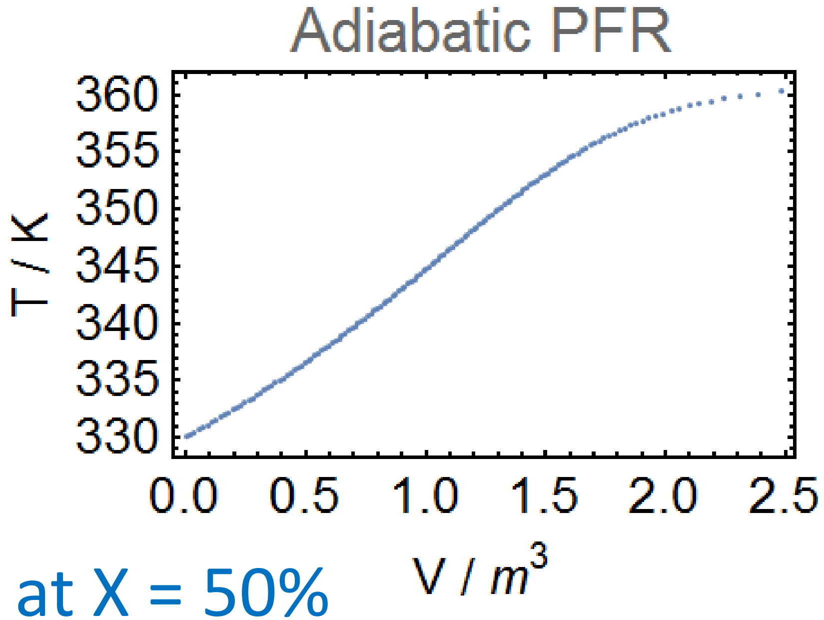

V_{PFR} = 1.408 m^3 at X = 50%

Levenspiel Plot

```
(* Want to plot Fa0/-ra as the y axis,
first define it *)

LevYpfr[x_] := 15.77 / (kf[T[x]] * ((1 - x) - x / Kc[T[x]]))
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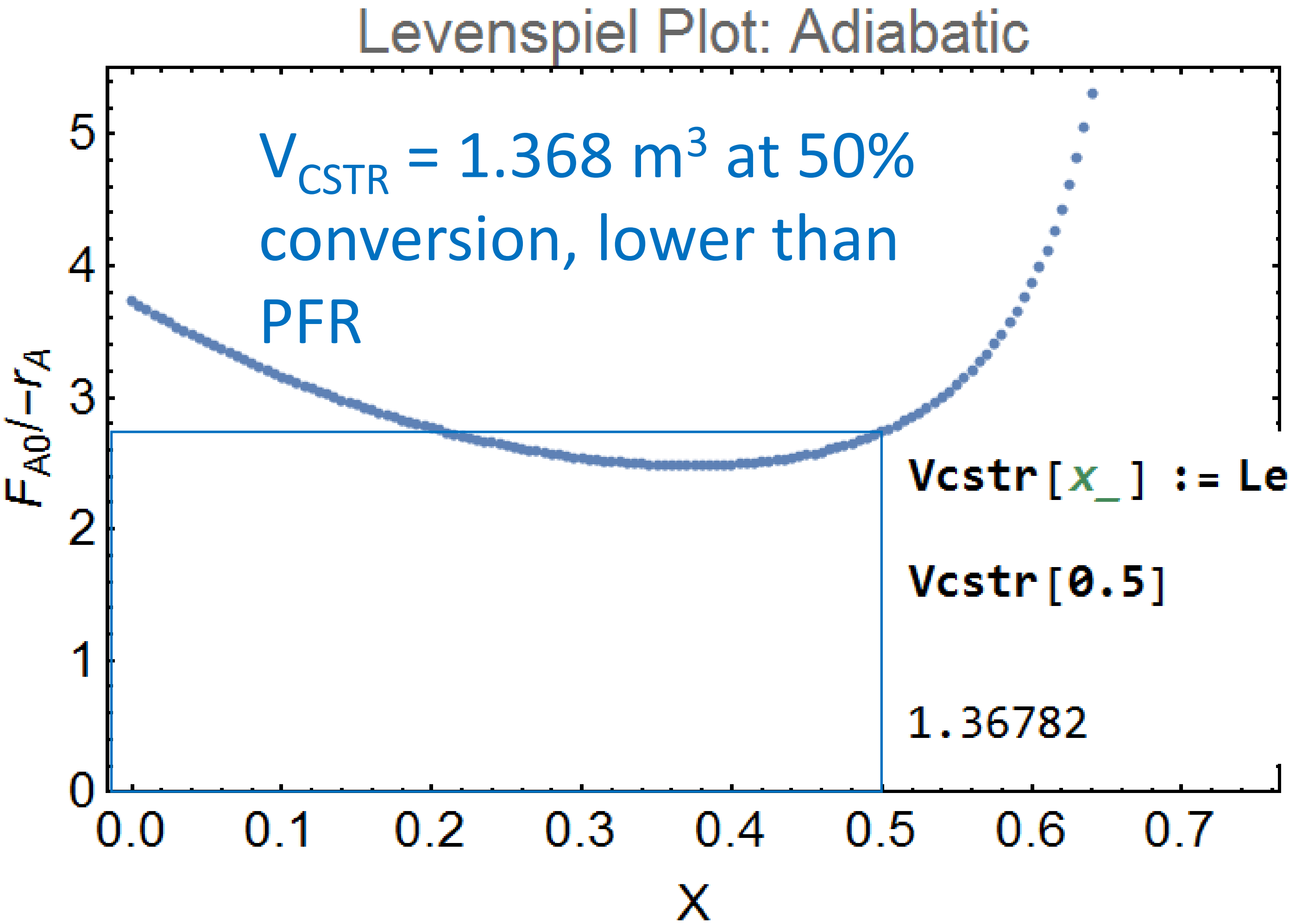


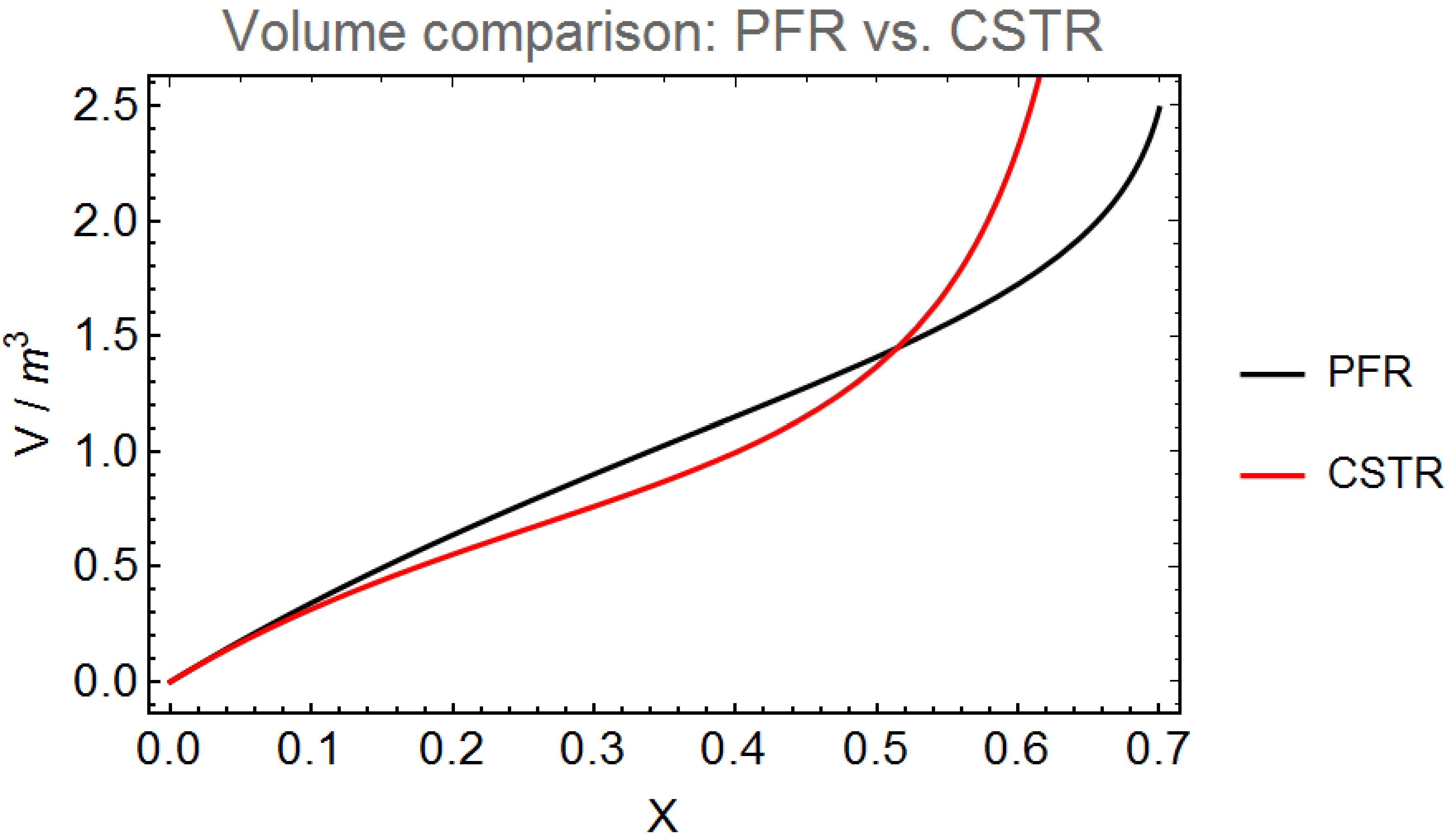
V_{CSTR} = 1.368 m^3 at 50% conversion, lower than PFR

```
Vcstr[x_] := LevYpfr[x] * x

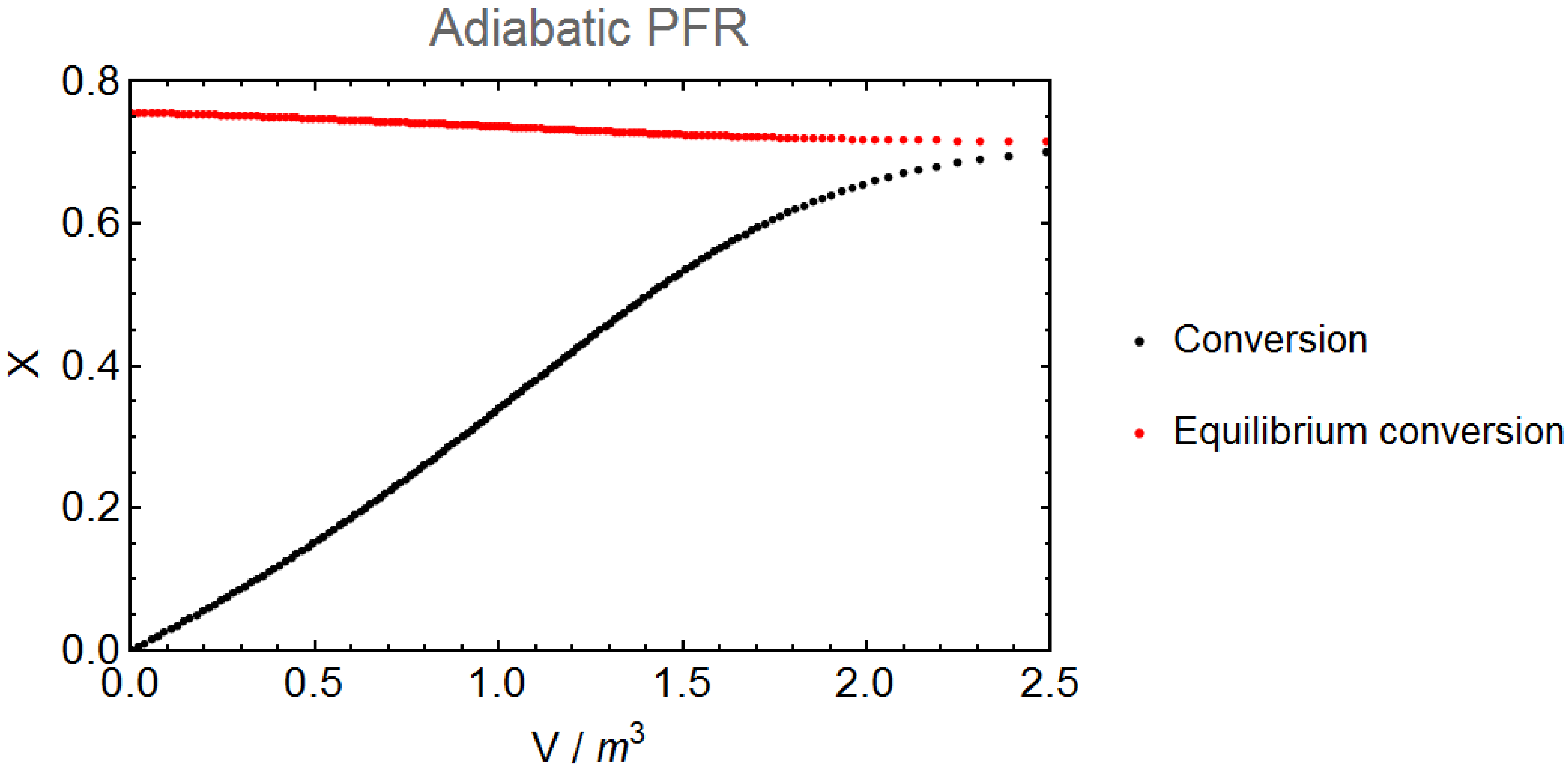
Vcstr[0.5]

1.36782
```

Plotting the V_{CSTR} and V_{PFR} functions together to compare volumes at different conversions



Plotting the equilibrium vs. reactor conversion as a function of reactor volume.



```
(* What is the equilibrium conversion through the reactor *)
ListPlot[Table[{Vpfr[x], Kc[T[x]] / (1 + Kc[T[x]])}, {x, 0, 0.7, 0.005}],
 FrameStyle → Directive[Black, FontColor → Black], BaseStyle → {FontSize → 14},
 Frame → True, FrameLabel → {"V / m3", "Xeq"},
 PlotLabel → "Adiabatic PFR: Equilibrium Conversion"]
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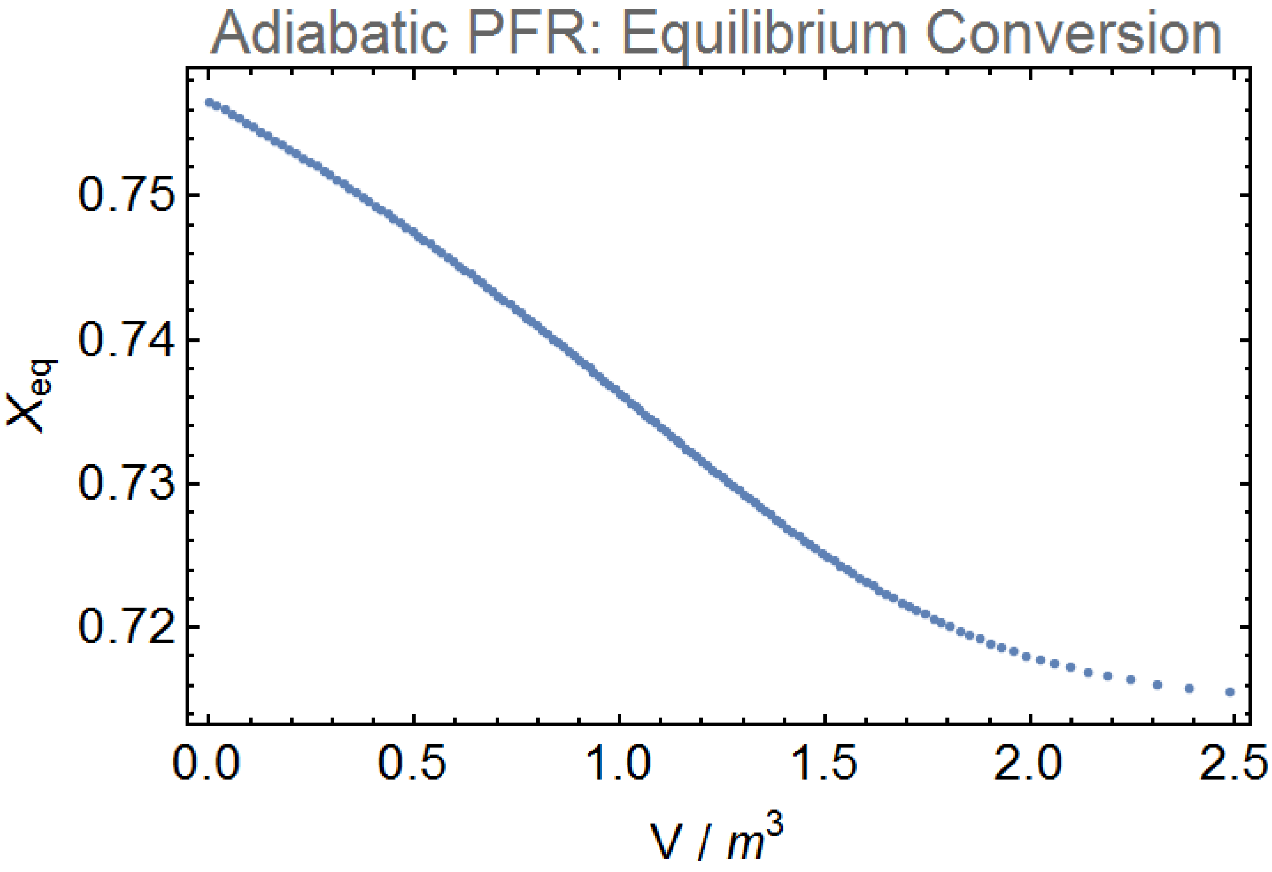

For the reaction:

$$A \rightleftarrows B$$

$$K_C = \frac{C_{B,eq}}{C_{A,eq}}$$

$$X_{eq} = \frac{K_C}{1 + K_C}$$