ChE 344
Reaction Engineering and Design

Lecture 13: Tuesday, February 22, 2022

Non-isothermal reactor design-Energy balance and adiabatic reactors

Reading for today's Lecture: Chapter 11.1-11.3

Reading for Lecture 14: Chapter 11.4-11.5

Lecture 13: Non-isothermal Reactor Design
Related Text: Chapter 11.1-11.4

Due to the strong dependence of the reaction rate on temperature, we need to know how to properly account for temperature change in non-isothermal reactors.

Some key definitions from **thermodynamics**:

$C_{P,i}$ is heat capacity of species i (in this class we assume to be constant, and assume no phase changes)

H_i is molar enthalpy of species i, in units of J/mol

$$H_i(T) = H_i(T_1) + (T - T_1)C_{P,i}$$

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

$$\Delta H_{rxn} = \sum \nu_i H_i$$

For example reaction $aA + bB \rightarrow cC + dD$:

$$\Delta H_{rxn} = -aH_A - bH_B + cH_C + dH_D$$

$$\Delta C_P = -aC_{P,A} - bC_{P,B} + cC_{P,C} + dC_{P,D}$$

The Energy Balance

Open system, sums refer to all species i in the reactor.

$$\sum_{\forall i} F_i E_i|_{in} - \sum_{\forall i} F_i E_i|_{out} + \dot{Q} - \dot{W} = \frac{d\hat{E}_{sys}}{dt}$$

For most chemical reactors (kinetic and potential energy are small, no shear stress):

$$\sum F_{i0}H_{i0} - \sum F_i H_i + \dot{Q} - \dot{W}_s = \frac{d\hat{E}_{sys}}{dt}$$

For systems that can be solved in terms of conversion, X, assuming X = 0 at inlet, and no phase change:

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

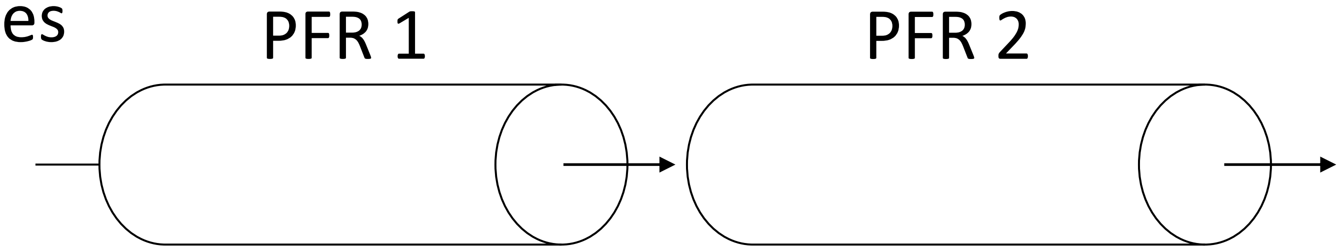
For adiabatic reactors in this class:

- No heat added/removed from reactor
- No shaft work
- Steady state

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

Last time, **multiple reactions**

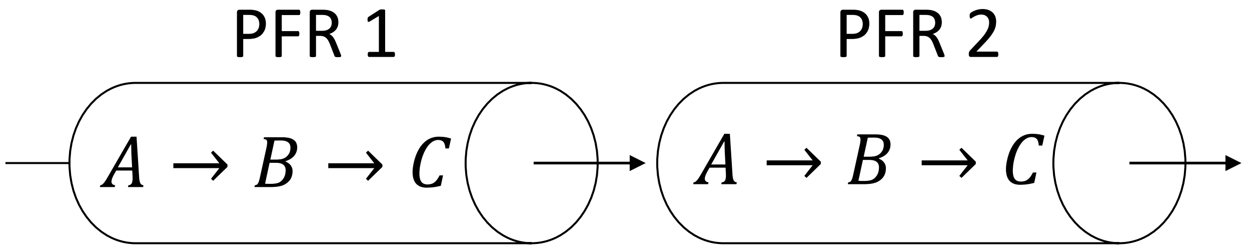
Reac**tors** in series



Reac**tions** in series

$$A \xrightarrow{k_1} B \qquad B \xrightarrow{k_2} C$$

Reac**tions** in series in reac**tors** in series



Other types of multiple reactions:

Complex	Parallel	Independent
$A + B \rightarrow C + D$	$A \xrightarrow{k_1} D$	$A \xrightarrow{k_1} D$
$A + C \rightarrow E$	$A \xrightarrow{k_2} U$	$B \xrightarrow{k_2} U$
$E \rightarrow G$		

Example: Batch reactor-want to maximize N_B:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

If we assume our batch reactor is constant volume: $C_j = N_j/V_0$

Mole balance on each species

$$\frac{dC_A}{dt} = r_A \qquad \frac{dC_B}{dt} = r_B \qquad \frac{dC_C}{dt} = r_C$$

Rates on each species

$$r_A = r_{1A} + r_{2A} \qquad r_B = r_{1B} + r_{2B} \qquad r_C = r_{1C} + r_{2C}$$

$$-r_{1A} = r_1 = k_1 C_A \qquad r_{1B} = r_1 = k_1 C_A \qquad r_{1C} = 0$$

$$r_{2A} = 0 \qquad -r_{2B} = r_2 = k_2 C_B \qquad r_{2C} = r_2 = k_2 C_B$$

$$\boxed{r_A = -k_1 C_A} \qquad \boxed{r_B = k_1 C_A - k_2 C_B} \qquad \boxed{r_C = k_2 C_B}$$

Stoich. For batch $N_A + N_B + N_C = N_{A0} + N_{B0} + N_{C0}$

$C_j = N_j/V_0$ $\quad C_A + C_B + C_C = C_{A0} + C_{B0} + C_{C0}$

Combine: Constant V batch design and rate laws

$$\frac{dC_A}{dt} = -k_1 C_A$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$

$$\frac{dC_C}{dt} = k_2 C_B$$

Can replace with mole balance

Solve first equation: Analytically or numerically

$$\frac{1}{-k_1 C_A} dC_A = dt$$

$$C_A = C_{A0} e^{-k_1 t}$$

Can plug this into balance for B:

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} e^{-k_1 t}$$

Can solve to get (through Laplace transform or integrating factor)

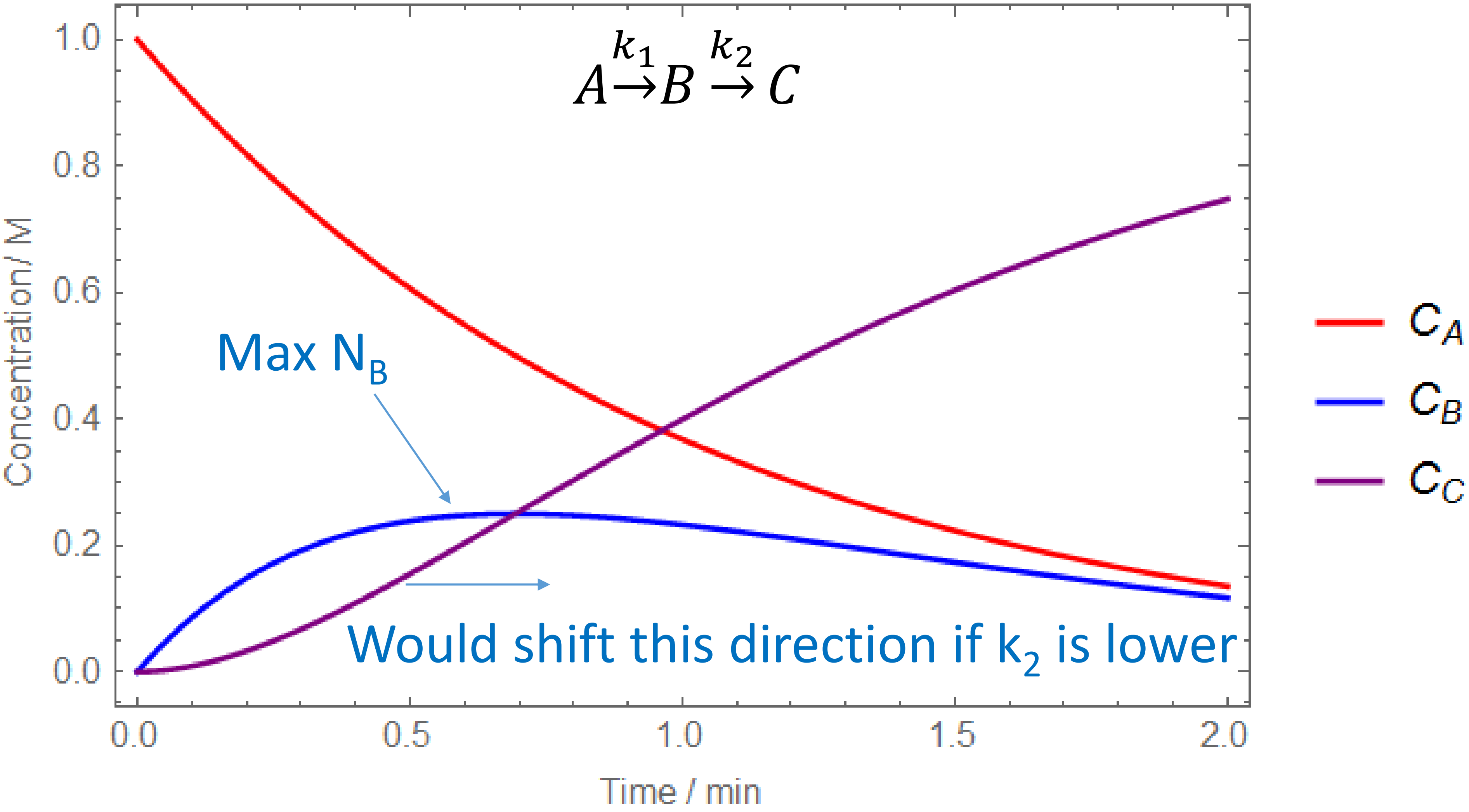
$$C_B = \left(\frac{C_{A0} k_1}{k_1 - k_2} + C_{B0}\right) e^{-k_2 t} - \frac{C_{A0} k_1}{k_1 - k_2} e^{-k_1 t}$$

And by mass balance:

$$\begin{aligned} C_C &= C_{A0} + C_{B0} + C_{C0} - C_A - C_B \\ &= C_{A0} + C_{B0} + C_{C0} - C_{A0} e^{-k_1 t} \\ &\quad - \left[\left(\frac{C_{A0} k_1}{k_1 - k_2} + C_{B0}\right) e^{-k_2 t} - \frac{C_{A0} k_1}{k_1 - k_2} e^{-k_1 t}\right] \end{aligned}$$

If $C_{A0} = 1$ M, $C_{B0} = C_{C0} = 0$ M, $k_1 = 1\ \text{min}^{-1}$, $k_2 = 2\ \text{min}^{-1}$

Series reaction



$A \xrightarrow{k_1} B \xrightarrow{k_2} C$

Max N_B

Would shift this direction if k_2 is lower

Could also numerically solve

Then have:

Skipped in class

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} e^{-k_1 t}$$

Can solve by taking Laplace transform

$$F(s) = \int_0^\infty f(t) e^{-st} dt$$

$$\widehat{C_B}(s) = \mathcal{L}\{C_B(t)\} = \int_0^\infty C_B(t) e^{-st} dt$$

$$\mathcal{L}\left\{\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} e^{-k_1 t}\right\}$$

$$\int_0^\infty \frac{dC_B}{dt} e^{-st} dt + k_2 \widehat{C_B}(s) = k_1 C_{A0} \int_0^\infty e^{-k_1 t} e^{-st} dt$$

$$\int_0^\infty \frac{dC_B}{dt} e^{-st} dt + k_2 \widehat{C_B}(s) = k_1 C_{A0} \frac{1}{k_1 + s}$$

Recall for Laplace transforms:

Skipped in class

$$\mathcal{L}\{f'(t)\} = sF(s) - f(0)$$

$$s\widehat{C_B}(s) - C_{B0} + k_2\widehat{C_B}(s) = k_1 C_{A0}\frac{1}{k_1 + s}$$

$$\widehat{C_B}(s) = \frac{sC_{B0} + k_1(C_{A0} + C_{B0})}{(s + k_1)(s + k_2)}$$

$$\mathcal{L}^{-1}\left\{\widehat{C_B}(s) = \frac{sC_{B0} + k_1(C_{A0} + C_{B0})}{(s + k_1)(s + k_2)}\right\}$$

$$C_B = \mathcal{L}^{-1}\left\{\frac{sC_{B0} + k_1(C_{A0} + C_{B0})}{(s + k_1)(s + k_2)}\right\}$$

$$= \mathcal{L}^{-1}\left\{\frac{k_1 C_{A0}}{(s + k_1)(s + k_2)}\right\} + \mathcal{L}^{-1}\left\{\frac{C_{B0}}{s + k_2}\right\}$$

Some definitions:

Skipped in class

$$\mathcal{L}^{-1}\left\{\frac{1}{s-a}\right\} = e^{at}$$

$$C_B = k_1 C_{A0}\mathcal{L}^{-1}\left\{\frac{1}{(s+k_1)(s+k_2)}\right\} + C_{B0}e^{-k_2 t}$$

$$\mathcal{L}^{-1}\left\{\frac{b}{(s-a)^2-b^2}\right\} = e^{at}\sinh(bt)$$

$$\mathcal{L}^{-1}\left\{\frac{b}{s^2-2as+a^2-b^2}\right\} = e^{at}\sinh(bt)$$

$$\mathcal{L}^{-1}\left\{\frac{1}{s^2+(k_2+k_1)s+k_2k_1}\right\} = \frac{e^{at}\sinh(bt)}{b}$$

$$k_2+k_1 = -2a; a = -\frac{k_2+k_1}{2}$$

$$a^2 - b^2 = k_2 k_1; b = \frac{k_1 - k_2}{2}$$

Skipped in class

$$C_B = k_1 C_{A0} \left[\frac{2}{k_1 - k_2} e^{-\frac{k_2 + k_1}{2} t} \frac{e^{\frac{k_1 - k_2}{2} t} - e^{-\frac{k_1 - k_2}{2} t}}{2} \right] + C_{B0} e^{-k_2 t}$$

$$C_B = \left(\frac{C_{A0} k_1}{k_1 - k_2} + C_{B0} \right) e^{-k_2 t} - \frac{C_{A0} k_1}{k_1 - k_2} e^{-k_1 t}$$

Isothermal reactors:

$T = T_0$ or more rigorously $\frac{dT}{dV} = 0$ $\frac{dT}{dW} = 0$ $\frac{dT}{dt} = 0$

Two questions:

1. Why would a reactor not be isothermal?
2. What's the big deal if its not isothermal?

Short answers:

1. Many reactions are exothermic or endothermic, and so T of reactants/products can change with conversion
2. A lot of the parameters in our reactor design algorithm are dependent on temperature!

$$k = Ae^{-\frac{E_a}{RT}}$$

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

For gases:

$$v = v_0 \frac{F_T}{F_{T0}} \frac{T}{T_0} \frac{P_0}{P}$$

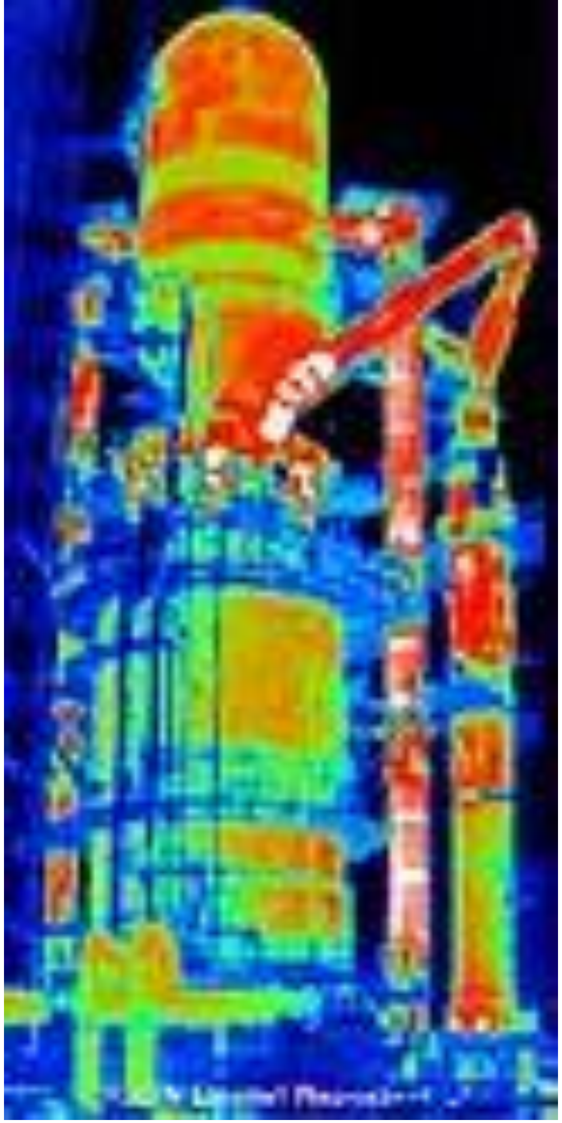
Real reactors

In real systems, often the isothermal assumption breaks down. Imagine an *endo*thermic reaction, where as the reaction proceeds the T_{fluid} decreases, lowering k and slowing r_A.

Even worse, imagine an *exo*thermic reaction where the T increases, increasing k, increasing r_A, which increases T more!

We can model this using energy/heat balances.

$$\frac{dT}{dV} \neq 0$$



Thermal image of cat. cracker (long chain hydrocarbons to shorter chains)

Dealing with temperature effects is conceptually similar to pressure drop, because we end with coupled equations.

PBR combined equation example:

$$\frac{dX}{dW} = \frac{-r_A'}{F_{A0}} = \frac{kC_A}{F_{A0}} = \frac{Ae^{-\frac{E_a}{RT(X)}}C_{A0}(1-X)}{F_{A0}(1+\varepsilon X)}\frac{T_0}{T(X)}\overset{p(W)}{\boxed{\frac{P(W)}{P_0}}}$$

For pressure drop, we used the Ergun equation to link P or p and W, and then we could solve the coupled equations.

For non-isothermal reactors, we will link T to:

- X (for adiabatic reactors)
- X and V (for reactors with heat exchangers)

using the Energy Balance

We will start with the simpler **adiabatic reactors** (no heat entering/leaving) for next several lectures (up to Midterm 2)

Going to start off with giving the simplified equation for <u>single</u> reaction: Then will show simplifications required to use it

Adiabatic CSTR, PFR, Batch or PBR Energy Balance:

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

$C_{P,i}$ is the heat capacity of species *i*

θ_i is the initial/inlet ratio of species *i* to limiting reactant

T_0 is the inlet (flow) or initial (batch) temperature

T is the temperature at conversion *X*

T_{ref} is a reference temperature (T_R in book)

ΔC_P is the change in heat capacities of associated reaction

ΔH_{rxn} is the heat of reaction (ΔH_{Rx} in book)

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

Often $\Delta H_{rxn}\left(T_{ref}\right) \gg \Delta C_P\left(T - T_{ref}\right)$

$$X \approx \frac{\sum \theta_i C_{P,i}[T - T_0]}{-[\Delta H_{rxn}]}$$

$$X \propto \pm[T - T_0]$$

Conversion is linear with temperature (sign related to the sign of heat of reaction).

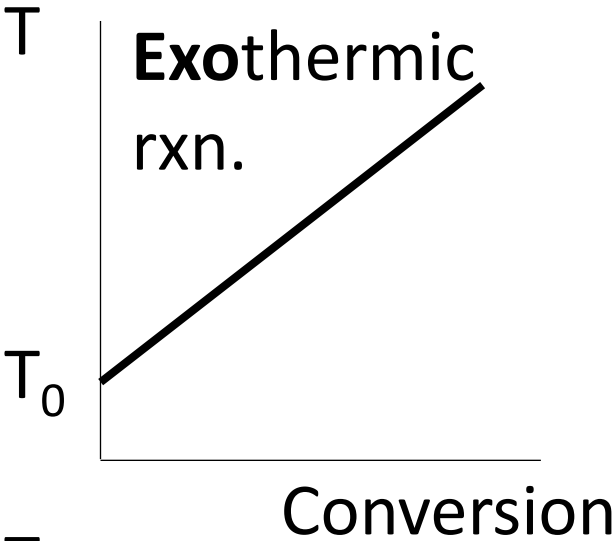
If ΔC_P=0

$$T = T_0 + \frac{-[\Delta H_{rxn}]X_{EB}}{\sum \theta_i C_{P,i}}$$

Discuss with your neighbors:

Which of the following would you expect to be correct for an adiabatic system?

[✓ **A)**]



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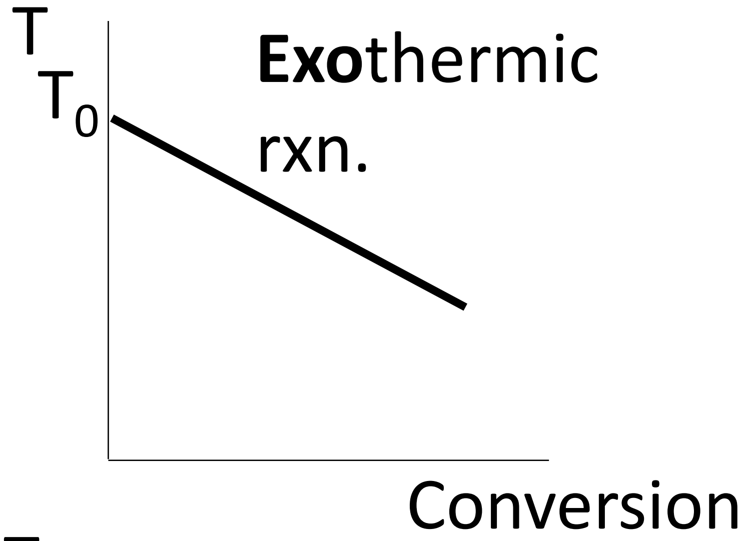

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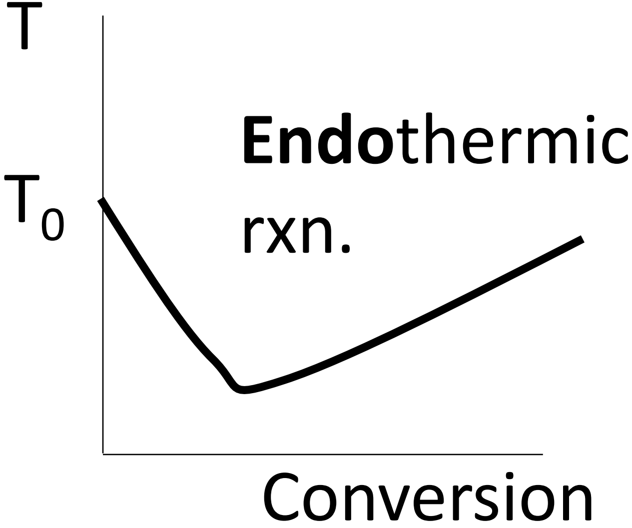

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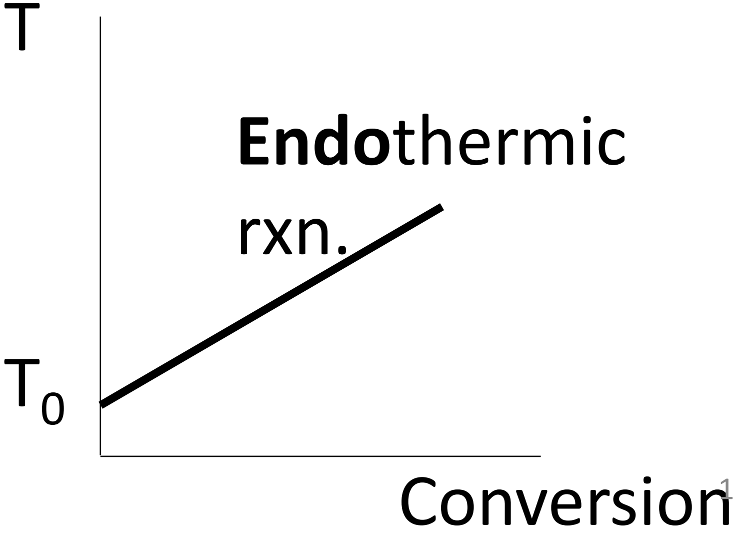
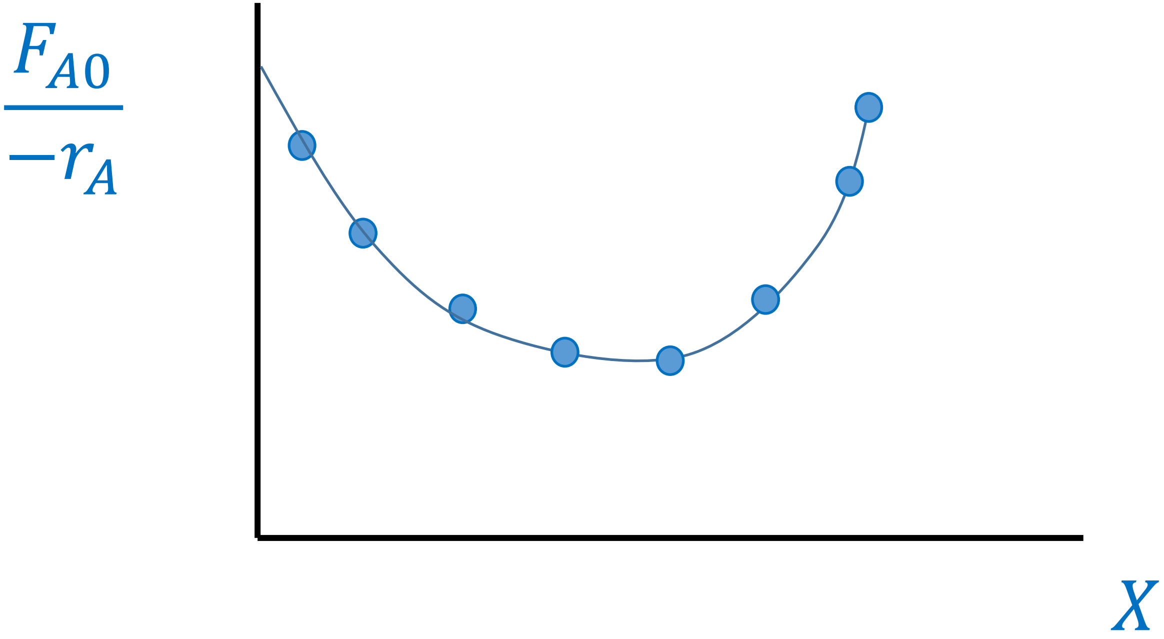


Possible ways to solve for adiabatic reactors:

Levenspiel plots

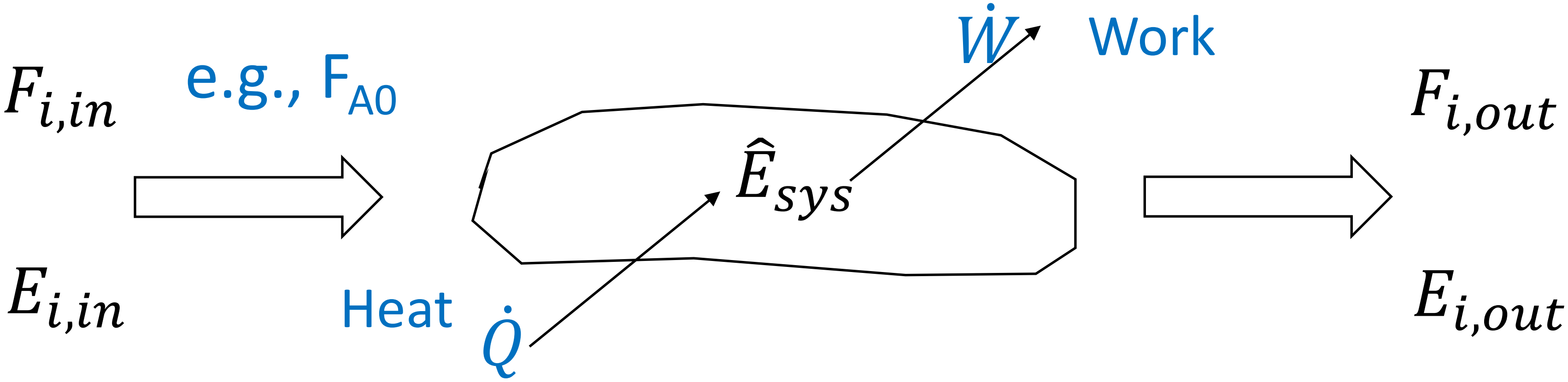
Choose X → calculate T → calculate *k* → calculate $-r_A$ → $\frac{F_{A0}}{-r_A}$



Alternative (recommended if able)

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.)

Energy balance is similar to how we did a mole balance.



$F_{i,in}$ e.g., F_{A0}

$E_{i,in}$

Heat $\dot{Q}$

$\hat{E}_{sys}$

$\dot{W}$ Work

$F_{i,out}$

$E_{i,out}$

$$\sum_{\forall i} F_i E_i \Big|_{in} - \sum_{\forall i} F_i E_i \Big|_{out} + \dot{Q} - \dot{W} = \frac{d\hat{E}_{sys}}{dt}$$

Rate of energy **added** to system by mass flow **into** system

\-

Rate of energy **leaving** system by mass flow **out** of system

\+

Rate of flow of heat **to** system **from** surr-oundings

\-

Rate of work **done by** system **on** surr-oundings

=

Rate of accumulation of energy within system

$[J/s]$

E_i is energy of species *i*, and has units of J/mol.

Note $\hat{E}_{sys}$ is total energy (not of just one species)

$$E_i = \underbrace{U_i}_{internal} + \underbrace{\frac{u^2}{2}}_{kinetic\ energy} + \underbrace{gz}_{potential\ energy}$$

Kinetic energy and potential energy are generally small for chemical reactors and so $E_i = U_i$

Separating $\dot{W}$ into flow work and other work ($\dot{W}_{shaft}$ or $\dot{W}_s$)

$$\dot{W} = -\sum F_i P\tilde{V}_i\Big|_{in} + \sum F_i P\tilde{V}_i\Big|_{out} + \dot{W}_s$$

No shear stress

$\tilde{V}_i$ specific molar volume

Plugging in to get new energy balance equation:

$$\sum_{\forall i} F_i\left(U_i + P\tilde{V}_i\right)\Big|_{in} - \sum_{\forall i} F_i\left(U_i + P\tilde{V}_i\right)\Big|_{out} + \dot{Q} - \dot{W}_s = \frac{d\hat{E}_{sys}}{dt}$$

Enthalpy of a species *i*:

$$H_i = U_i + P\tilde{V}_i \qquad [J/mol]$$

$$\underbrace{\sum F_i H_i\Big|_{in}}_{\sum F_{i0} H_{i0}} - \sum F_i H_i\Big|_{out} + \dot{Q} - \dot{W}_s = \frac{d\hat{E}_{sys}}{dt}$$

$$aA + bB \rightarrow cC + dD$$

Rewrite in terms of limiting reactant A

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

$$F_i = F_{A0}(\theta_i + \nu_i X)$$

v vs. ν_i: *v* is volumetric flow rate (italic ‘v’), ν_i is stoichiometric coefficient (‘nu’)

$$\theta_i \equiv \frac{F_{i0}}{F_{A0}} \qquad F_B = F_{A0}\left(\theta_B - \frac{b}{a}X\right) \qquad \nu_B = -\frac{b}{a}$$

Substituting in info from stoichiometry:

$$\sum F_{A0}\theta_i H_{i0} - \sum F_{A0}(\theta_i + \nu_i X)H_i + \dot{Q} - \dot{W}_s = \frac{d\hat{E}_{sys}}{dt}$$

$$= F_{A0}\sum(\theta_i[H_{i0} - H_i] - \nu_i H_i X) + \dot{Q} - \dot{W}_s$$

$$F_{A0}\sum \theta_i[H_{i0} - H_i] - F_{A0}X\boxed{\sum \nu_i H_i} + \dot{Q} - \dot{W}_s = \frac{d\hat{E}_{sys}}{dt}$$

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

How do you get H_i? Usually will know H_i for some reference (solid), and can convert to conditions you are interested in.

$$H_i(T) =$$

Heat capacity of solid

$$H_i^\circ\left(T_{ref}\right) + \int_{T_{ref}}^{T_m} C_{P,S_i}\,dT + \underbrace{\Delta H_{m,i}(T_m)}_{melting} + \int_{T_m}^{T_v} C_{P,L_i}\,dT$$

of liquid

$$+\ \underbrace{\Delta H_{v,i}(T_v)}_{vaporization} + \int_{T_v}^{T} C_{P,g_i}\,dT$$

of gas

So also need the energy of reaction to be shifted from T_{ref} by heat capacities.

In a simple case:

1. No phase change
2. C_P are constant with temperature

$$\Delta H_{rxn}(T) = \Delta H_{rxn}\left(T_{ref}\right) + \sum \nu_i C_{P,i}\left(T - T_{ref}\right)$$

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

$$\Delta H_{rxn}(T) = \Delta H_{rxn}\left(T_{ref}\right) + \Delta C_P\left(T - T_{ref}\right)$$

Energy balance (just rewriting it from above):

$$F_{A0} \sum \theta_i [H_{i0} - H_i] - F_{A0} X \sum \nu_i H_i + \dot{Q} - \dot{W}_s = \frac{d\hat{E}_{sys}}{dt}$$

In addition for our limiting assumptions of no phase change and constant heat capacities with temperature:

$$H_i = H_{i0} + C_{P,i}(T - T_0)$$

$$H_{i0} - H_i = -C_{P,i}(T - T_0)$$

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?

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

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

$$C_{P,NH_3} = 8.92\, cal/mol\ H_2 \cdot K$$

$$C_{P,N_2} = 6.984\, cal/mol\ H_2 \cdot K$$

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

$$H^\circ_{H_2}(25°C) = 0$$

$$H^\circ_{N_2}(25°C) = 0$$

[✓ 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

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

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

<u>Adiabatic reactor</u> (additional assumptions)

1. $\dot{Q} = 0$
2. $\dot{W}_{shaft} = 0$
3. Steady state: $\frac{d\hat{E}_{sys}}{dt} = 0$

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

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

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.)