ChE 344
Reaction Engineering and Design

Lecture 20: Tuesday, March 29, 2022

Unsteady State Reactor Design + Safety, cont.

Reading for today's Lecture: Chapter 13

Reading for Lecture 21: Chapter 9

Lecture 20: Unsteady state reactor energy balance with CSTR startup example
Related Text: Chapter 13

From the energy balance we have used before we can get equations to describe the change in temperature with respect to time, which will need to be coupled to the mole balance equations, as a change in temperature will affect the reaction rates.
One example for adiabatic batch reactor with no shaft work, constant heat capacity with T and no phase change:

$$T = T_0 + \frac{[-\Delta H_{rxn}(T_0)]X}{C_{P0} + \Delta C_P X}$$

For <u>multiple reactions</u>:

$$\frac{dT}{dt} = \frac{\overbrace{\sum_{i=1}^{n} r_{ij} V \Delta H_{rxn,ij}}^{\dot{Q}_{gs}} - \left[\overbrace{F_{A0}\sum_{j=1}^{m} \theta_j C_{P,j}(T-T_0) + \left(UA(T-T_a)\right)}^{\dot{Q}_{rs}}\right]}{\sum_{j=1}^{m} N_j C_{P,j}}$$

Here n is the number of reactions, and m is the number of species in the reactor.

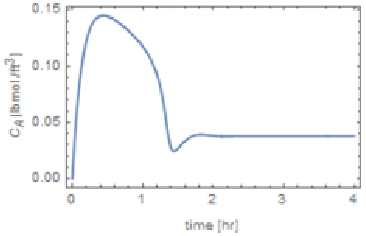
<u>Unsteady state CSTR (CSTR during startup):</u>
Mole balance and rate law can give us expressions for the change in concentrations with time for constant volumetric flow rate in and out of reactor (V is constant):

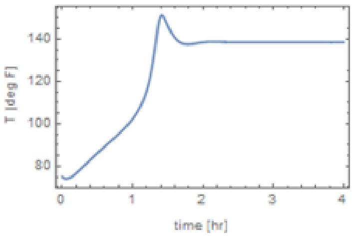
$$C_{i0}v_0 - C_i v_0 - \nu_i r_A V = \frac{dC_i V}{dt}$$

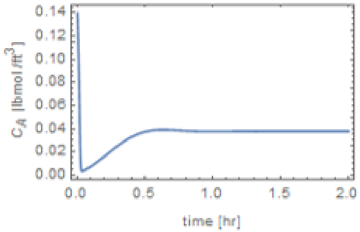
Using energy balance (here coolant flow rate is not necessarily large):

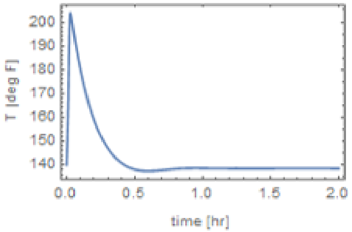
$$\frac{\sum F_{i0}\left[C_{P,i}(T_0 - T)\right] + \Delta H_{rxn} r_A V + \dot{m}_c C_{P,c}(T_{a1} - T)\left(1 - \exp\left[\frac{-UA}{\dot{m}_c C_{P,c}}\right]\right)}{\sum N_i C_{P,i}} = \frac{dT}{dt}$$

Depending on <u>initial</u> (t=0) conditions, steady state is reached but in different pathways (time profiles):





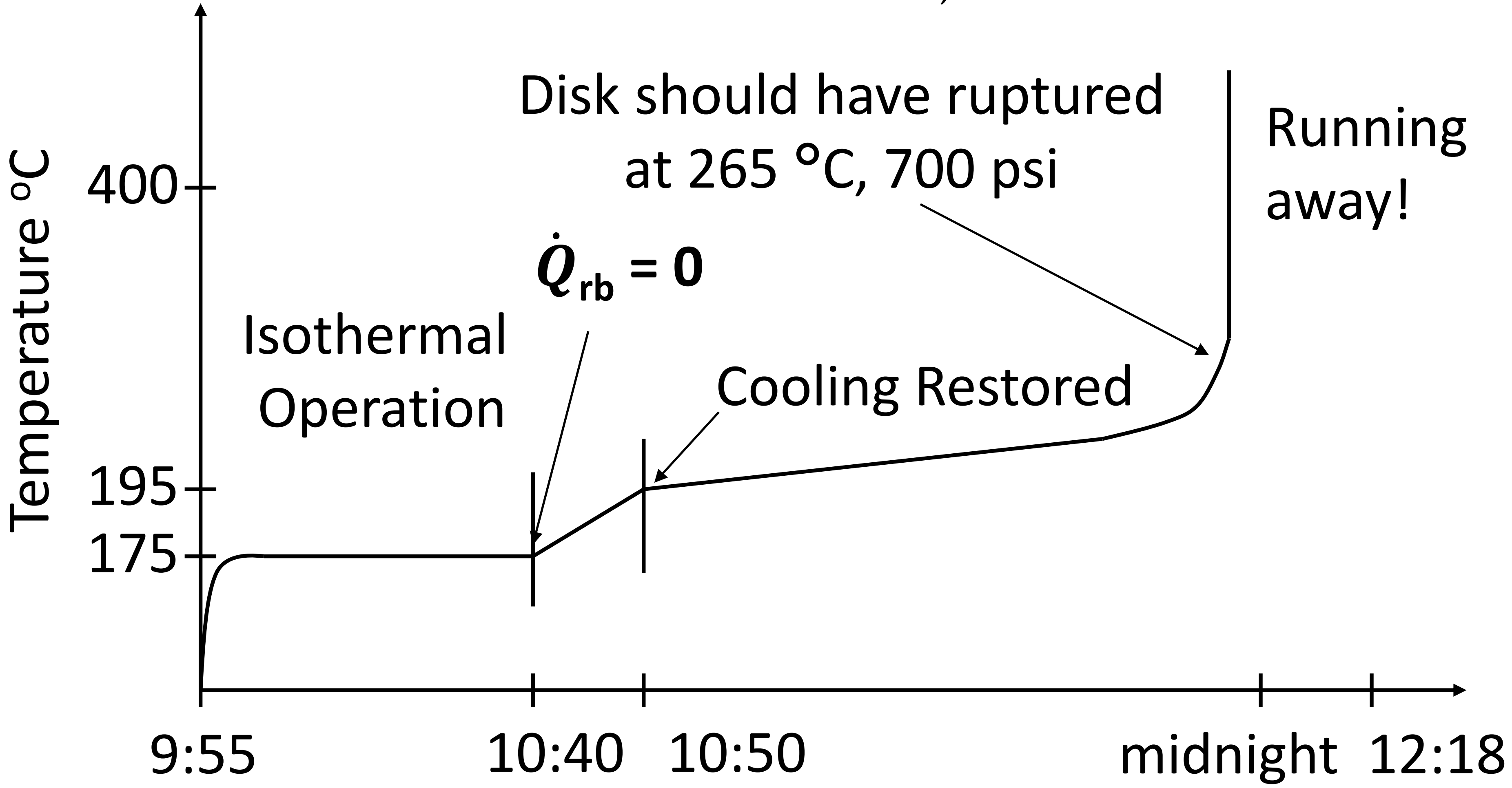




On Thursday: Safety for exothermic reactions

Reactor ‘runaway’ if this is too large

$$\frac{dT}{dt} = \frac{\overbrace{(\Delta H_{rxn})(r_A V)}^{\dot{Q}_{gb}\ or\ \dot{Q}_{gs}} - \left[\overbrace{F_{A0}\sum \theta_i C_{P,i}\,(T - T_0) + \overset{\dot{Q}_{rb}}{\boxed{\left(UA(T - T_a)\right)}}}^{\dot{Q}_{rs}}\right]}{\sum N_i C_{P,i}}$$



Isothermal Operation

$\dot{Q}_{rb} = 0$

Cooling Restored

Disk should have ruptured at 265 °C, 700 psi

Running away!

Overview for **unsteady state, non-isothermal** reactors

- Derive the unsteady state energy balance
- How to solve a batch, adiabatic reactor
- Unsteady state reactors with heat exchange
  - CSTRs/semi-batch reactors
    - $\dot{Q}_{gs}$ (generated heat from reaction)
    - $\dot{Q}_{rs}$ (removal from feed + heat exchanger)
  - Batch reactors with heat exchange
    - $\dot{Q}_{gb}$ (generated heat from reaction)
    - $\dot{Q}_{rb}$ (removal from heat exchanger only)
  - Multiple reactions
- Example: CSTR during startup (approach to steady-state)

Discuss with your neighbors:

Thinking about our energy balance below:

$$\frac{dT}{dt} = \frac{\overbrace{(\Delta H_{rxn})(r_A V)}^{\dot{Q}_{gs}} - \left[\overbrace{F_{A0}\sum \theta_i C_{P,i}\,(T - T_0) + \big(UA(T - T_a)\big)}^{\dot{Q}_{rs}}\right]}{\sum N_i C_{P,i}}$$

Which of the following are true?

I. $\dot{Q}_{gs}$ can never be negative — False, if endothermic

II. $\dot{Q}_{rs}$ can never be negative — False, e.g. $T < T_a$

III. $\dot{Q}_{rs}$ is > than $\dot{Q}_{rb}$ if $T > T_0$ — True, CSTR inlet effectively removing heat

A) I, II, and III

B) I

[✓ C) III]

D) None of them

Energy balance for unsteady state systems

$$\underbrace{\sum_{i=1}^{m} F_i H_i\Big|_{in}}_{\sum F_{i0}H_{i0}} - \sum_{i=1}^{m} F_i H_i\Big|_{out} + \dot{Q} - \dot{W}_s = \frac{d\hat{E}_{sys}}{dt}$$

$$\hat{E}_{sys} = \sum N_i U_i = \sum N_i\left(H_i - P\tilde{V}_i\right) = \sum N_i H_i - P\sum N_i \tilde{V}_i$$

Often the PV term is neglected, and if there are no spatial variations:

- CSTR (when not at steady-state)
- Batch or semi-batch

$$\frac{d\hat{E}_{sys}}{dt} = \frac{d\sum N_i H_i}{dt} = \sum N_i \frac{dH_i}{dt} + H_i \frac{dN_i}{dt}$$

Recall relation of enthalpy and heat capacity:
$$\frac{dH_i}{dt} = C_{P,i}\frac{dT}{dt}$$

Mole balance on species *i*:
$$F_{i0} - F_i - \nu_i r_A V = \frac{dN_i}{dt}$$

Plugging in to get accumulation term:

$$\frac{d\hat{E}_{sys}}{dt} = \sum N_i\left(C_{P,i}\frac{dT}{dt}\right) + H_i(F_{i0} - F_i - \nu_i r_A V)$$

Unsteady state energy balance:

$$\sum F_{i0}H_{i0} - \sum \cancel{F_iH_i} + \dot{Q} - \dot{W}_s$$

$$= \sum\left[N_iC_{P,i}\frac{dT}{dt} + H_iF_{i0} - \cancel{H_iF_i} - H_i\nu_i r_A V\right]$$

$$\sum F_{i0}H_{i0} + \dot{Q} - \dot{W}_s = \sum \left[N_i C_{P,i} \frac{dT}{dt} + H_i F_{i0} \right] - \Delta H_{rxn} r_A V$$

$$\sum F_{i0}[H_{i0} - H_i] + \Delta H_{rxn} r_A V + \dot{Q} - \dot{W}_s = \frac{dT}{dt} \sum N_i C_{P,i}$$

Gives energy balance on a transient CSTR, batch, semi-batch:

$$\frac{\sum F_{i0}[H_{i0} - H_i] + \Delta H_{rxn} r_A V + \dot{Q} - \dot{W}_s}{\sum N_i C_{P,i}} = \frac{dT}{dt}$$

If no phase change and heat capacities are constant with T,

$H_{i0} - H_i = C_{P,i}(T_0 - T)$ and we can simplify further to:

$$\frac{\sum F_{i0}\left[C_{P,i}(T_0 - T)\right] + \Delta H_{rxn} r_A V + \dot{Q} - \dot{W}_s}{\sum N_i C_{P,i}} = \frac{dT}{dt}$$

Batch reactor:

$$\frac{\Delta H_{rxn} r_A V + \dot{Q} - \dot{W}_s}{\sum N_i C_{P,i}} = \frac{dT}{dt}$$

Couple with mass balance:

$$\frac{dN_i}{dt} = r_i V$$

Adiabatic batch reactor with no shaft work:

$$\frac{\Delta H_{rxn} r_A V}{\sum N_i C_{P,i}} = \frac{dT}{dt}$$

If instead of time
we used space time
it could be PFR

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

$$\frac{dN_A}{dt} = \frac{d(N_{A0}(1 - X))}{dt} = -N_{A0}\frac{dX}{dt}$$

Combine design equation into energy balance:

$$\Delta H_{rxn}\left(-N_{A0}\frac{dX}{dt}\right)=\frac{dT}{dt}\sum N_iC_{P,i}$$

$$N_i=N_{A0}(\theta_i+\nu_iX)$$

$$-N_{A0}\Delta H_{rxn}\frac{dX}{dt}=N_{A0}\frac{dT}{dt}\sum(\theta_i+\nu_iX)C_{P,i}$$

In previous lectures we have defined:

$$C_{P0}\equiv\sum\theta_iC_{P,i}$$

$$\Delta C_P=\sum\nu_iC_{P,i}$$

So energy balance is now:

$$-\Delta H_{rxn}\frac{dX}{dt} = \frac{dT}{dt}\left(C_{P0} + \Delta C_P X\right)$$

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

$$-\left(\Delta H_{rxn}\left(T_{ref}\right) + \Delta C_P\left(T - T_{ref}\right)\right)\frac{dX}{dt} = \frac{dT}{dt}\left(C_{P0} + \Delta C_P X\right)$$

$$\int_0^X \frac{dX}{C_{P0} + \Delta C_P X} = \int_{T_0}^T \frac{dT}{-\left(\Delta H_{rxn}\left(T_{ref}\right) + \Delta C_P\left(T - T_{ref}\right)\right)}$$

Take definite integrals

$$\int_c^d \frac{dx}{ax+b} = \frac{1}{a}\ln(ad+b) - \frac{1}{a}\ln(ac+b)$$

*Skipped in class

$$\frac{1}{\Delta C_P}(\ln(C_{P0}+\Delta C_P X)-\ln(C_{P0}))$$
$$=\frac{1}{\Delta C_P}\left[\ln\left(-\left(\Delta H_{rxn}\left(T_{ref}\right)-T_{ref}\Delta C_P\right)-\Delta C_P T\right)\right.$$
$$\left.-\ln\left(-\left(\Delta H_{rxn}\left(T_{ref}\right)-T_{ref}\Delta C_P\right)-\Delta C_P T_0\right)\right]$$

After integration, multiply both by ΔC_P, know that quotient rule for ln is that subtracting logs is division inside the log, then take exponential of both sides:

$$\cancel{1} + \frac{\Delta \cancel{C}_P X}{C_{P0}}$$

*Skipped step in class

$$= \frac{-\left(\Delta H_{rxn}\left(T_{ref}\right) - T_{ref}\Delta C_P\right) - \Delta C_P T_0 - \Delta C_P T + \Delta C_P T}{-\left(\Delta H_{rxn}\left(T_{ref}\right) - T_{ref}\Delta C_P\right) - \Delta C_P T}$$

$$= \cancel{1} - \frac{\Delta \cancel{C}_P (T - T_0)}{\left(\Delta H_{rxn}\left(T_{ref}\right) - T_{ref}\Delta C_P\right) + \Delta C_P T}$$

*Skipped step in class

$$\frac{X}{C_{P0}} = \frac{-(T - T_0)}{\left(\Delta H_{rxn}\left(T_{ref}\right) - T_{ref}\Delta C_P\right) + \Delta C_P T}$$

$$= \frac{T_0 - T}{\Delta H_{rxn}\left(T_{ref}\right) + (T - T_{ref})\Delta C_P} = \frac{T_0 - T}{\Delta H_{rxn}(T)}$$

Can put this into a form:

$$\frac{X\Delta H_{rxn}(T)}{C_{P0}} = T_0 - T$$

$$\frac{X(\Delta H_{rxn}(T_0) + (T - T_0)\Delta C_P)}{C_{P0}} = T_0 - T$$

$$T = T_0 - \frac{X(\Delta H_{rxn}(T_0) + (T - T_0)\Delta C_P)}{C_{P0}}$$

$$T + \frac{\Delta C_P X}{C_{P0}} T = T(1 + \frac{\Delta C_P X}{C_{P0}})$$

$$= T_0 - \frac{X(\Delta H_{rxn}(T_0) + (-T_0)\Delta C_P)}{C_{P0}}$$

$$T = \frac{C_{P0}T_0}{C_{P0}(1 + \frac{\Delta C_P X}{C_{P0}})} - \frac{X(\Delta H_{rxn}(T_0) + (-T_0)\Delta C_P)}{(1 + \frac{\Delta C_P X}{C_{P0}})C_{P0}}$$

$$T = \frac{C_{P0}T_0 + T_0\Delta C_P X}{C_{P0}(1 + \frac{\Delta C_P X}{C_{P0}})} - \frac{X\left(\Delta H_{rxn}(T_0)\right)}{\left(1 + \frac{\Delta C_P X}{C_{P0}}\right)C_{P0}}$$

$$= \frac{C_{P0}T_0 + T_0\Delta C_P X}{C_{P0} + \Delta C_P X} - \frac{X\left(\Delta H_{rxn}(T_0)\right)}{C_{P0} + \Delta C_P X}$$

$$= T_0 - \frac{X\left(\Delta H_{rxn}(T_0)\right)}{C_{P0} + \Delta C_P X}$$

*Skipped these steps in class

$$T = T_0 + \frac{[-\Delta H_{rxn}(T_0)]X}{C_{P0} + \Delta C_P X}$$

$$T = T_0 + \frac{[-\Delta H_{rxn}(T_0)]X}{C_{P0} + \Delta C_P X}$$

$$r_A V = -N_{A0}\frac{dX}{dt}$$

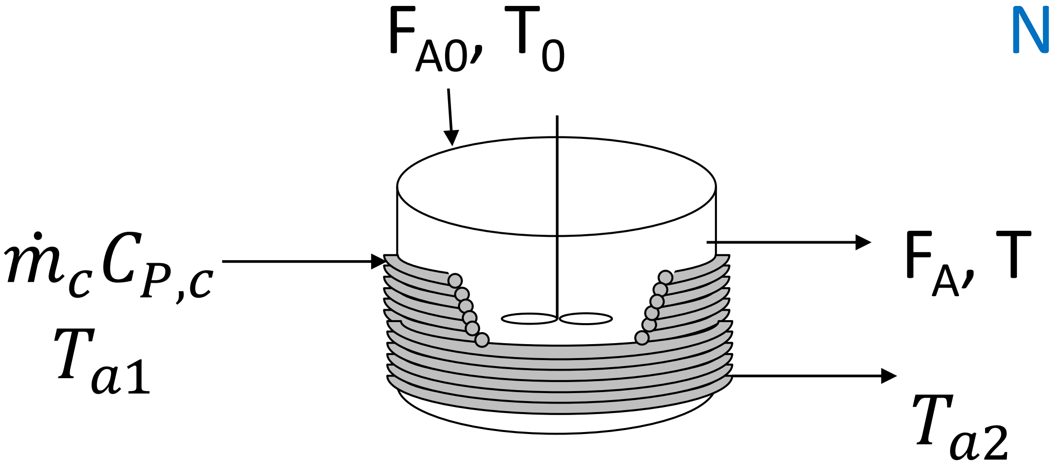
To solve, pick X, know a temperature from energy balance, solve for t.

$$dt = -N_{A0}\frac{dX}{r_A V}$$

Recall this was for adiabatic batch reactor with no shaft work

If there is heat transfer (non-adiabatic CSTR or semi-batch)

$$\frac{\sum F_{i0}\left[C_{P,i}(T_0 - T)\right] + \Delta H_{rxn} r_A V + \dot{Q}}{\sum N_i C_{P,i}} = \frac{dT}{dt}$$



No shaft work

From heat exchanger using a coolant (from Lecture 17) realizing that heat exchanger on a CSTR, semi-batch or batch are essentially the same:

$$\dot{Q} = \dot{m}_c C_{P,c}(T_{a1} - T)\left(1 - \exp\left[\frac{-UA}{\dot{m}_c C_{P,c}}\right]\right) = -\dot{Q}_{rb}$$

For large flow rates of coolant: $T_{a1} \approx T_{a2} \approx T_a$

$$\dot{Q} = UA(T_{a1} - T) = -\dot{Q}_{rb}$$

$$UA(T - T_a) = \dot{Q}_{rb}$$

Batch unsteady state with high coolant rates:

$$\frac{dT}{dt} = \frac{\Delta H_{rxn} r_A V - \left[-\dot{Q}\right]}{\sum N_i C_{P,i}} = \frac{\dot{Q}_{gb} - \dot{Q}_{rb}}{\sum N_i C_{P,i}}$$

CSTR or semi-batch unsteady state:

$$\frac{dT}{dt} = \frac{\Delta H_{rxn} r_A V - \left[\sum F_{i0}\left[C_{P,i}(T - T_0)\right] - \dot{Q}\right]}{\sum N_i C_{P,i}} = \frac{\dot{Q}_{gs} - \dot{Q}_{rs}}{\sum N_i C_{P,i}}$$

For multiple reactions:

Replace $\Delta H_{rxn} r_A$ term with

$$\sum_{i=1}^{n} r_{ij} \Delta H_{rxn,ij}$$

$$\dot{Q}_{gs} = \sum_{i=1}^{n} r_{ij} V \Delta H_{rxn,ij}(T)$$

This can change with T if $\Delta C_P \neq 0$

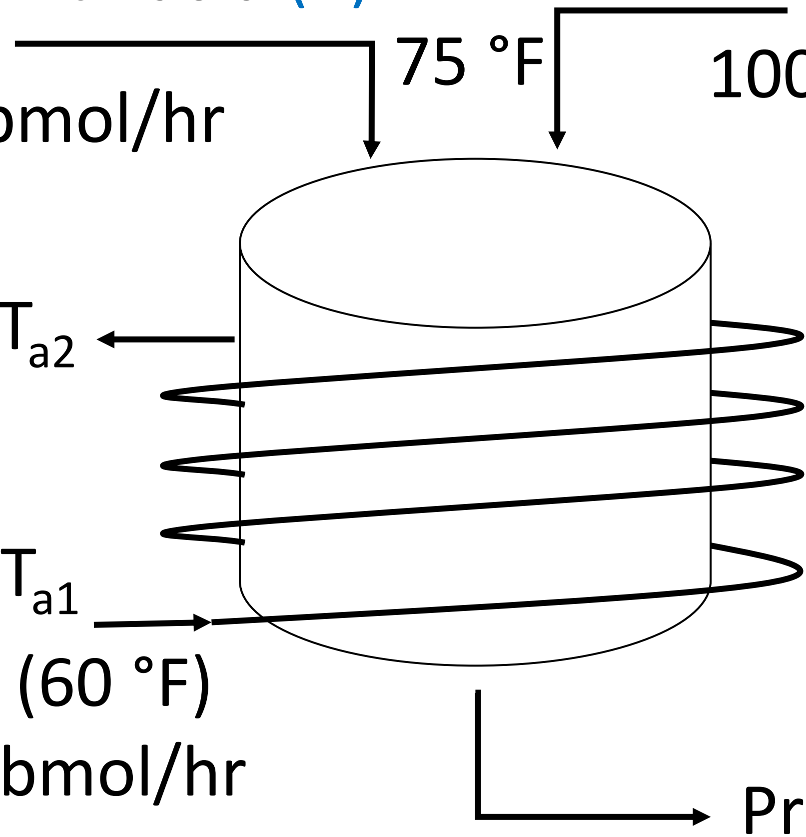
We can see that if there is only one reaction:

$$A \rightarrow B$$

$$\dot{Q}_{gs} = r_{1A} V \Delta H_{rxn,1A} = r_A V \Delta H_{rxn}$$

CSTR startup: Example problem

Propylene oxide plus water reacts to form propylene glycol in presence of inert methanol (with H_2SO_4 as catalyst). The reaction is first order in propylene oxide but zero-order in water.



Water with acid (B)

1000 lbmol/hr

75 °F

80 lbmol/hr propylene oxide(A)

100 lbmol/hr methanol (M)

T_{a2}

T_{a1}

Water (60 °F)

1000 lbmol/hr

$A + B \rightarrow C$

V_{CSTR} = 500 gallons

Products

Reactor starts with water with 0.1 wt% sulfuric acid at 75 °F

UA = 16000 Btu/hr·Rankine

$k(T) = 16.96\text{x}10^{12} \exp(-32400 \text{ Btu/lbmol}/RT) \text{ hr}^{-1}$

Heat of reaction = -36000 Btu/lbmol (exothermic)

Molar densities:

ρ_A = 0.923 lbmol/ft^3, ρ_B = **3.45 lbmol/ft^3**, ρ_C = 1.54 lbmol/ft^3

Initial conc. of B in CSTR

$C_{P,A}$=35 Btu/lbmol·R, $C_{P,B}$ =18 Btu/lbmol·R

$C_{P,C}$ =46 Btu/lbmol·R, $C_{P,M}$=19.5 Btu/lbmol·R

At time = 0 (initial conditions of variables C_i):

$C_A = 0$

$C_B = 3.45$ lbmol/ft^3

$C_C = 0$

$C_M = 0$

Questions:

1. What do T and C_A look like during startup?
2. Is steady state reached?
3. What happens if T(t=0) or C_A(t=0) are changed?
4. What are the conditions where we stay under practical stability limit of 180 Fahrenheit?

A + B → C in presence of inert methanol (M). First order in A, zero order in B. Write mole balance with rate law:

$$F_{i0} - F_i - \nu_i r_A V = \frac{dN_i}{dt}$$

$$C_{i0} v_0 - C_i v_0 - \nu_i r_A V = \frac{dC_i V}{dt}$$

Constant V

(1) $$\frac{C_{A0} - C_A}{\tau} - kC_A = \frac{dC_A}{dt}$$

(2) $$\frac{C_{B0} - C_B}{\tau} - kC_A = \frac{dC_B}{dt}$$

(3) $$\frac{C_{C0} - C_C}{\tau} + kC_A = \frac{dC_C}{dt}$$

(4) $$\frac{C_{M0} - C_M}{\tau} = \frac{dC_M}{dt}$$

Energy balance for unsteady state CSTR, no shaft work:

$$\frac{\sum F_{i0}\left[C_{P,i}(T_0 - T)\right] + \Delta H_{rxn} r_A V + \dot{Q}}{\sum N_i C_{P,i}} = \frac{dT}{dt} \qquad (5)$$

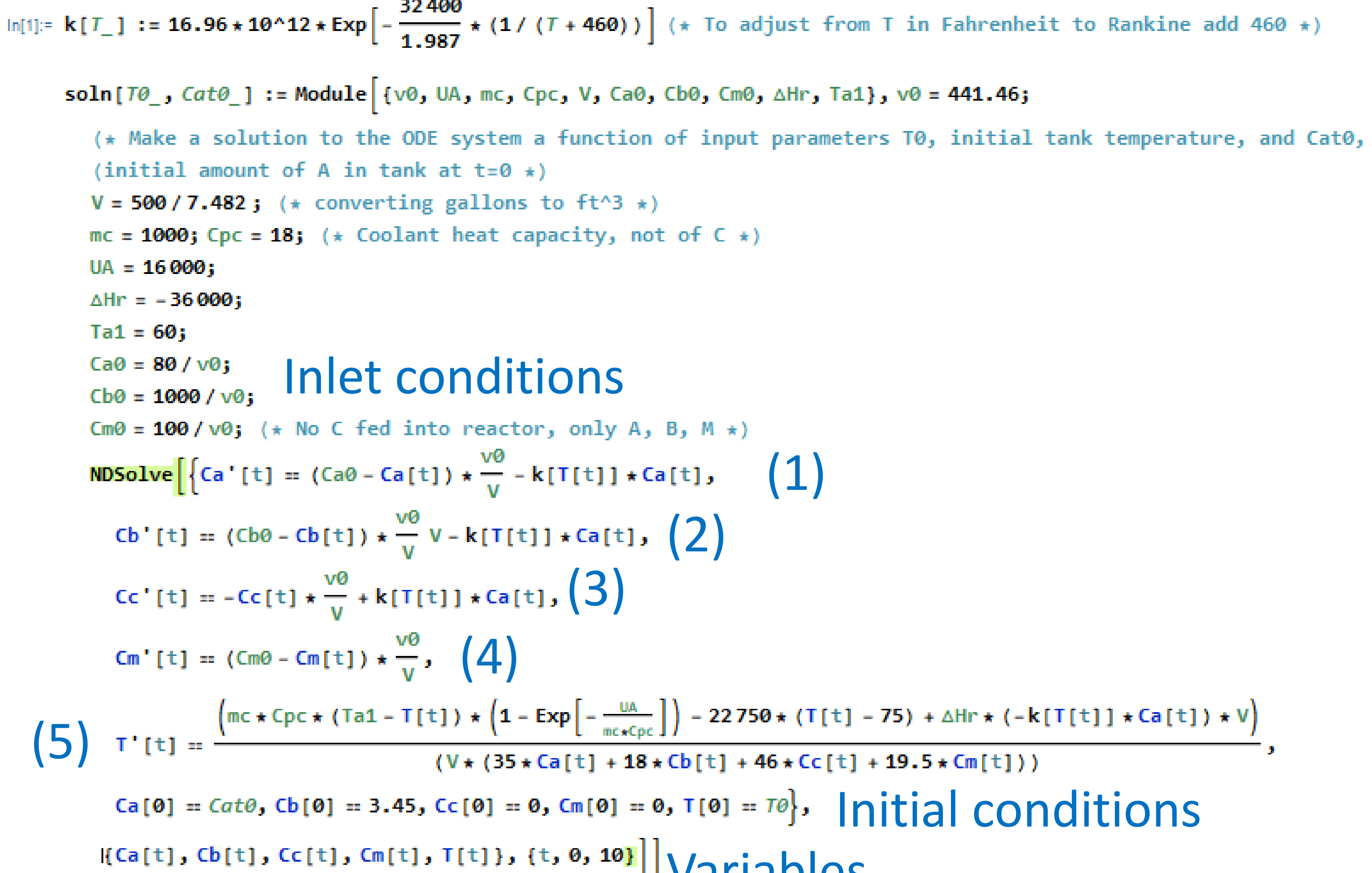
$$\dot{Q} = \dot{m}_c C_{P,c}(T_{a1} - T)\left(1 - \exp\left[\frac{-UA}{\dot{m}_c C_{P,c}}\right]\right)$$

Heat capacity of species in reactor:

$$\sum N_i C_{P,i} = V\left[C_A C_{P,A} + C_B C_{P,B} + C_C C_{P,C} + C_M C_{P,M}\right]$$

Heat removal of species flowing into reactor:

$$\sum F_{i0}\left[C_{P,i}(T_0 - T)\right] = -22750\ \mathrm{Btu/hr \cdot Rankine}\ (T - T_0)$$



```
In[1]:= k[T_] := 16.96 * 10^12 * Exp[-32400/1.987 * (1 / (T + 460))] (* To adjust from T in Fahrenheit to Rankine add 460 *)

  soln[T0_, Cat0_] := Module[{v0, UA, mc, Cpc, V, Ca0, Cb0, Cm0, ΔHr, Ta1}, v0 = 441.46;
    (* Make a solution to the ODE system a function of input parameters T0, initial tank temperature, and Cat0,
    (initial amount of A in tank at t=0 *)
    V = 500 / 7.482 ; (* converting gallons to ft^3 *)
    mc = 1000; Cpc = 18; (* Coolant heat capacity, not of C *)
    UA = 16000;
    ΔHr = -36000;
    Ta1 = 60;
    Ca0 = 80 / v0;
    Cb0 = 1000 / v0;
    Cm0 = 100 / v0; (* No C fed into reactor, only A, B, M *)
    NDSolve[{Ca'[t] == (Ca0 - Ca[t]) * v0/V - k[T[t]] * Ca[t],
      Cb'[t] == (Cb0 - Cb[t]) * v0/V V - k[T[t]] * Ca[t],
      Cc'[t] == -Cc[t] * v0/V + k[T[t]] * Ca[t],
      Cm'[t] == (Cm0 - Cm[t]) * v0/V,
      T'[t] == (mc * Cpc * (Ta1 - T[t]) * (1 - Exp[-UA/(mc*Cpc)]) - 22750 * (T[t] - 75) + ΔHr * (-k[T[t]] * Ca[t]) * V) / (V * (35 * Ca[t] + 18 * Cb[t] + 46 * Cc[t] + 19.5 * Cm[t])),
      Ca[0] == Cat0, Cb[0] == 3.45, Cc[0] == 0, Cm[0] == 0, T[0] == T0},
    {Ca[t], Cb[t], Cc[t], Cm[t], T[t]}, {t, 0, 10}]]
```

Inlet conditions

(1)

(2)

(3)

(4)

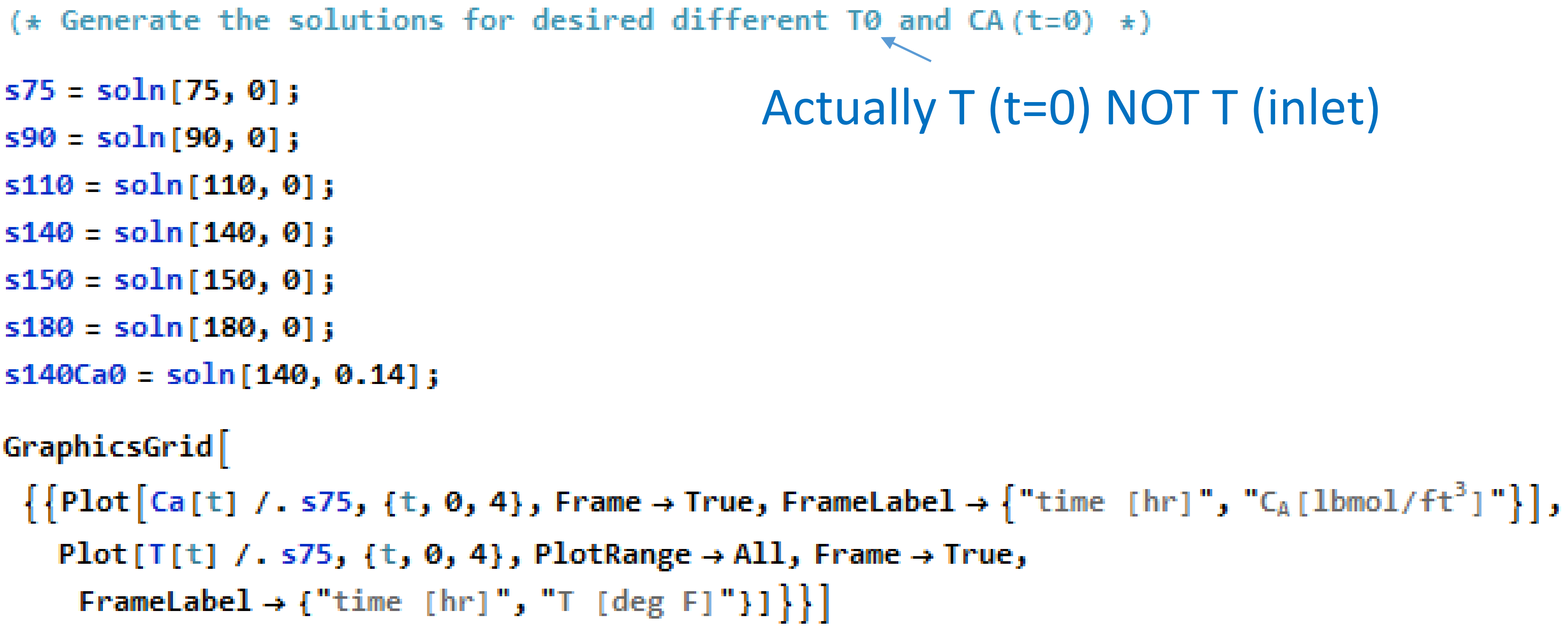
(5)

Initial conditions

Variables

$C_{P,A}$=35 Btu/lbmol·R, $C_{P,B}$ 18 Btu/lbmol·R

$C_{P,C}$ 46 Btu/lbmol·R, $C_{P,M}$=19.5 Btu/lbmol·R

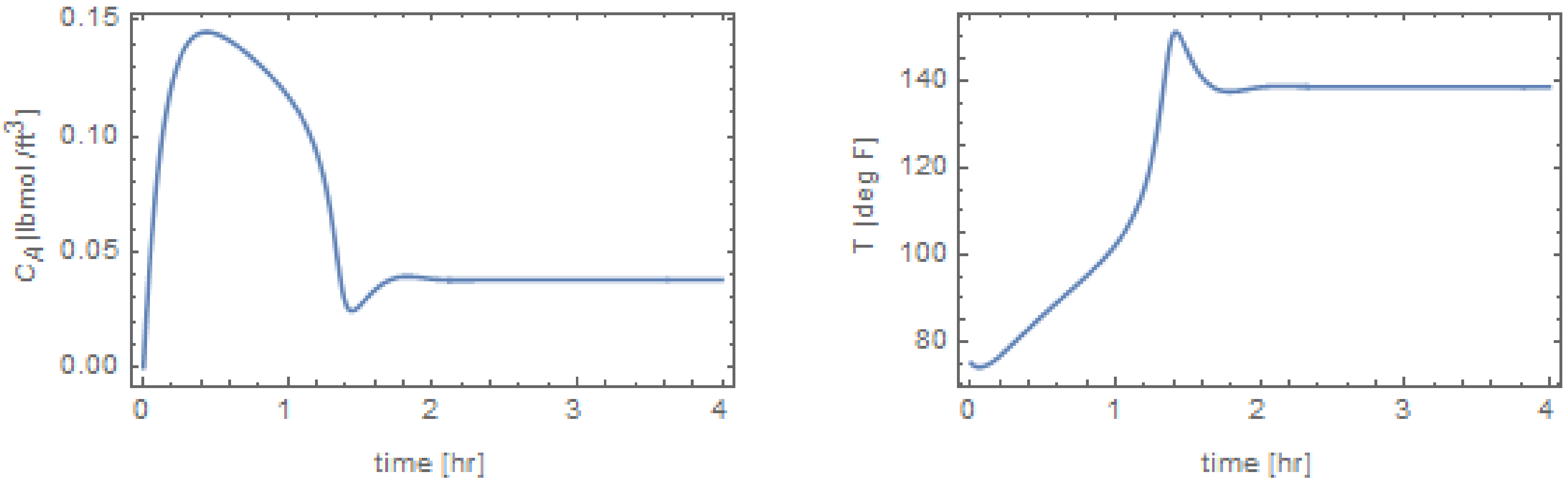


```
(* Generate the solutions for desired different T0 and CA(t=0) *)

s75 = soln[75, 0];
s90 = soln[90, 0];
s110 = soln[110, 0];
s140 = soln[140, 0];
s150 = soln[150, 0];
s180 = soln[180, 0];
s140Ca0 = soln[140, 0.14];

GraphicsGrid[
 {{Plot[Ca[t] /. s75, {t, 0, 4}, Frame → True, FrameLabel → {"time [hr]", "C_A[lbmol/ft^3]"}],
   Plot[T[t] /. s75, {t, 0, 4}, PlotRange → All, Frame → True,
    FrameLabel → {"time [hr]", "T [deg F]"}]}}]
```

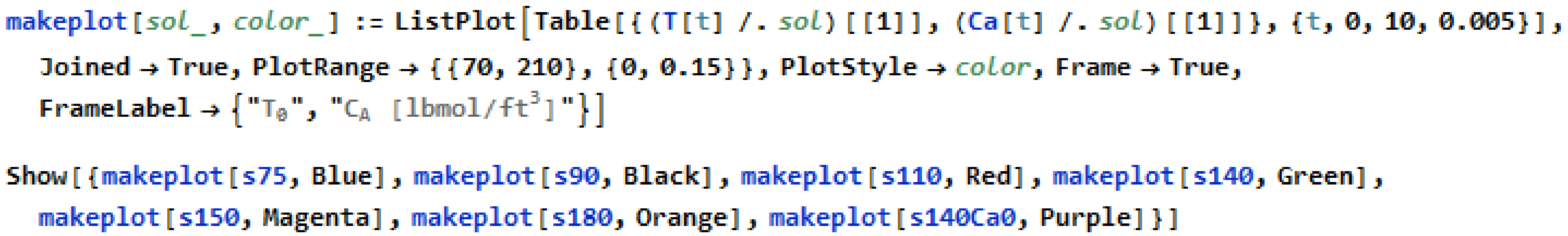
Actually T (t=0) NOT T (inlet)

T (t=0) = 75 F, C_A(t=0) = 0 lbmol/ft^3

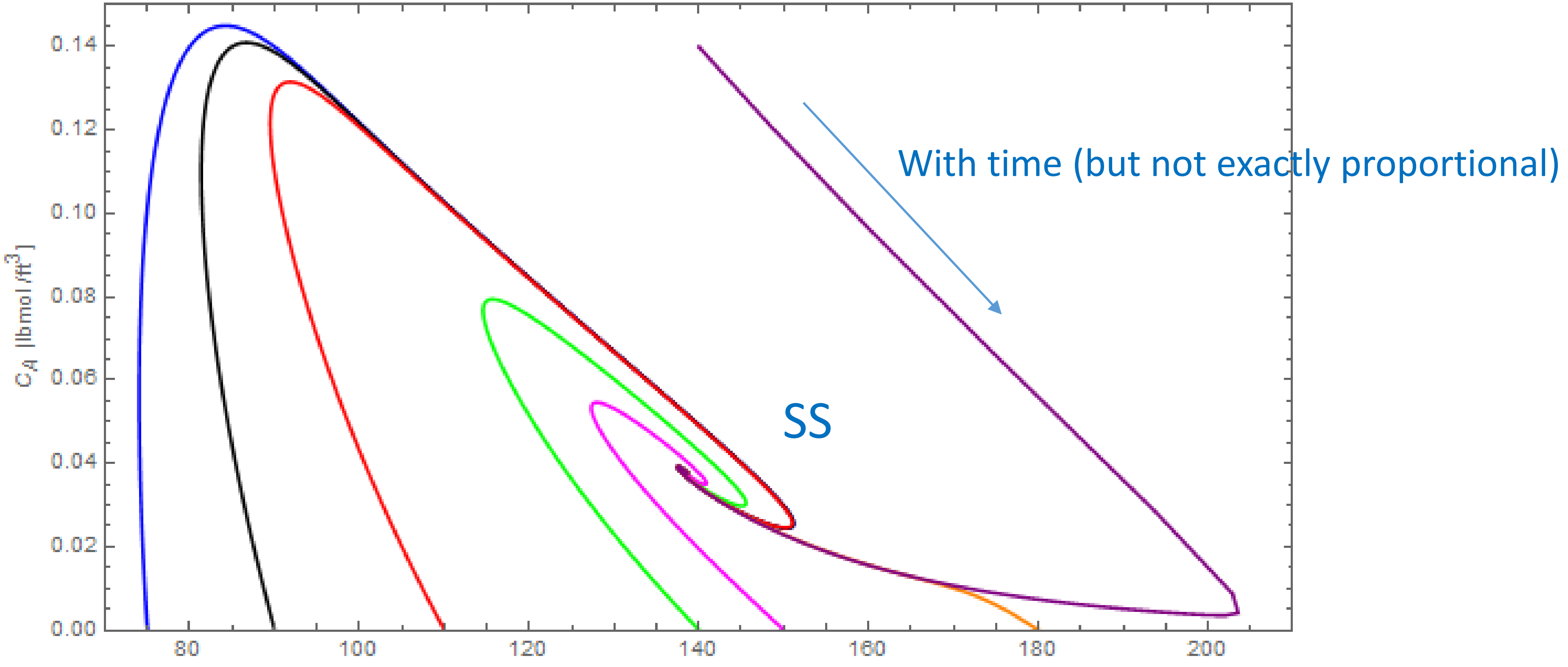
SS



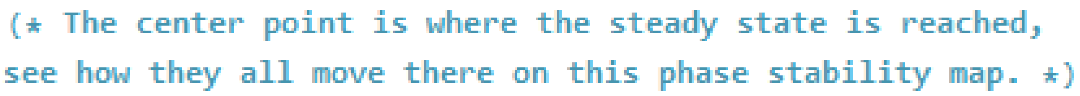
After initial time, C_A and T reach some steady state



```
makeplot[sol_, color_] := ListPlot[Table[{(T[t] /. sol)[[1]], (Ca[t] /. sol)[[1]]}, {t, 0, 10, 0.005}],
  Joined → True, PlotRange → {{70, 210}, {0, 0.15}}, PlotStyle → color, Frame → True,
  FrameLabel → {"T0", "CA [lbmol/ft3]"}]

Show[{makeplot[s75, Blue], makeplot[s90, Black], makeplot[s110, Red], makeplot[s140, Green],
  makeplot[s150, Magenta], makeplot[s180, Orange], makeplot[s140Ca0, Purple]}]
```



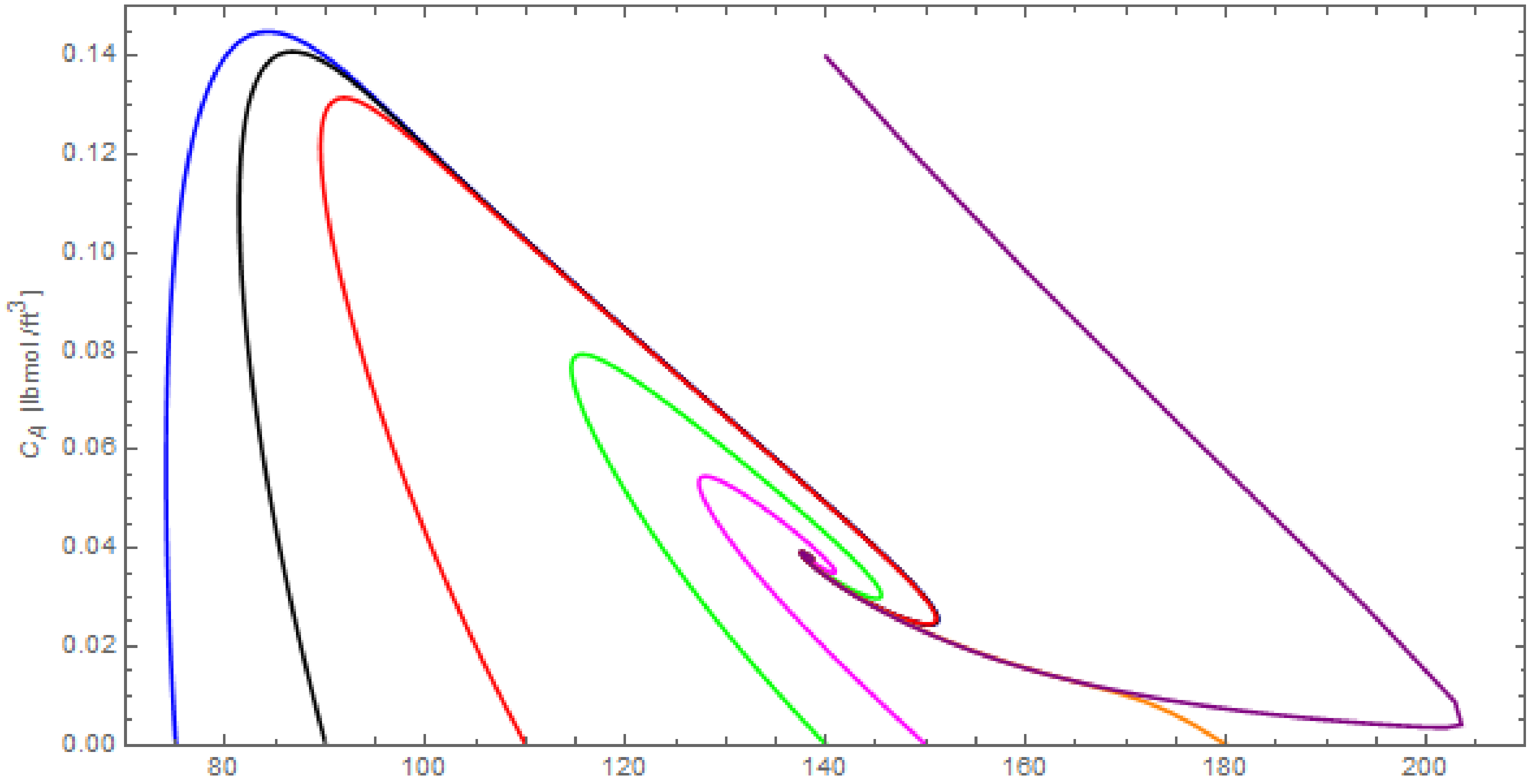
Temperature



```
(* The center point is where the steady state is reached,
see how they all move there on this phase stability map. *)
```

Discuss with your neighbors:

Which set of initial conditions for CSTR startup result in a temperature at some point that is greater than 200?



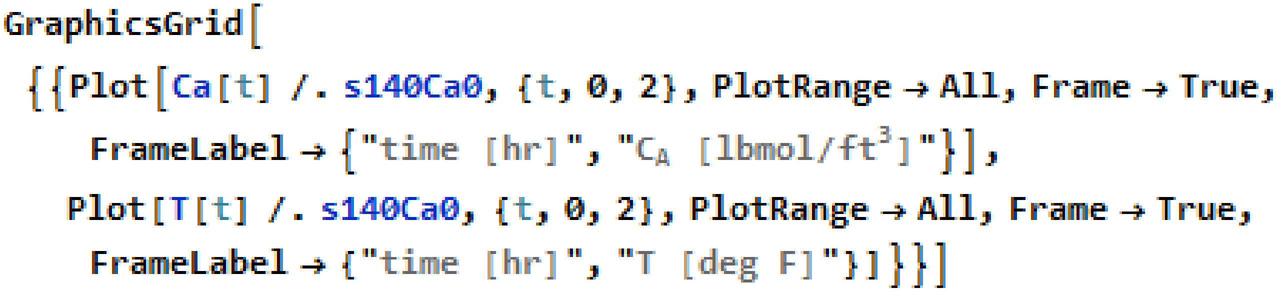
A) T(t=0) = 75 °F C_A (t=0) = 0

B) T(t=0) = 180 °F C_A (t=0) = 0

[✓ C) T(t=0) = 140 °F
C_A (t=0) = 0.14 lbmol/ft^3]

D) None of them

Following the purple line from above, we can look at the time behavior when T(t=0) is 140 °F and there is initially some propylene oxide ($C_A(t=0) = 0.14$ lbmol/ft^3). Notice the spike in temperature when starting. Reaches SS faster but more dangerous!



```
GraphicsGrid[
 {{Plot[Ca[t] /. s140Ca0, {t, 0, 2}, PlotRange → All, Frame → True,
    FrameLabel → {"time [hr]", "CA [lbmol/ft3]"}],
   Plot[T[t] /. s140Ca0, {t, 0, 2}, PlotRange → All, Frame → True,
    FrameLabel → {"time [hr]", "T [deg F]"}]}}]
```