

## Chemical Reaction Engineering - Part 15 - CSTR thermal effects, SS + Dynamic

Richard K. Herz, rherz@ucsd.edu, www.ReactorLab.net

Here we consider temperature as well as conversion in CSTRs. The contents of the reactor are well mixed and all at the same temperature. However, the temperature can change with time after input parameter values are changed, and steady state conditions will differ as parameter values are changed.

First we will consider steady-state conditions. Later we will see how the reactor can respond with time. A first-order reaction, essentially irreversible is considered. Physical properties are assumed to be constant. Even with such a simple system, complex behavior can result.

### Steady-state CSTR with thermal effects

Also refer back to CRE notes 09 for thermal effects in batch reactors and sections in CRE notes 13 for thermal effects in PFRs.

The simplified energy balance for a CSTR is

$$\rho C_{pm} V \frac{dT}{dt} = Q + W + \rho C_{pm} v (T_0 - T) + \Delta H_{rxn} r_A V$$

where  $\rho$  is fluid density ( $\text{kg/m}^3$ ),  $C_{pm}$  is mass-average heat capacity ( $\text{J/kg/K}$ ),  $Q$  ( $\text{J/s}$ ) is the rate of heat transfer across heat transfer surfaces (coils or jackets) into the reactor,  $W$  ( $\text{J/s}$ ) is the rate of non-PV work done on the reactor contents ("shaft work").  $T_0$  is the temperature of the inlet fluid and  $T$  is the temperature of the fluid in the CSTR.

The heat transfer term  $Q$  is

$$Q = UA(T_j - T)$$

At steady state and with negligible shaft work,

$$0 = UA(T_j - T) + \rho C_{pm} v (T_0 - T) + \Delta H_{rxn} r_A V$$

$$-UA(T_j - T) - \rho C_{pm} v (T_0 - T) = (-\Delta H_{rxn})(-r_A)V$$

$$-(UA T_j + \rho C_{pm} v T_0) + (UA + \rho C_{pm} v)T = (-\Delta H_{rxn})(-r_A)V$$

We need to solve this along with the steady-state component balance

$$\frac{dN_A}{dt} = 0 = F_{A0} - F_A + r_A V$$

$$(-r_A)V = F_{A0} - F_A$$

$$(-r_A)V = F_{A0} - F_{A0}(1 - X_A)$$

$$(-r_A)V = F_{A0} X_A$$

For example, for a first-order, essentially irreversible reaction,

$$r_A = -k C_A \quad \text{where} \quad k = A e^{-E_d/(RT)} \quad \text{or} \quad k = k_{T_{ref}} e^{-(E_d/R)(1/T - 1/T_{ref})}$$

The conversion is a function of the rate coefficients, which vary with  $T$ , and the space time:

$$X_A = \frac{C_{A0} - C_A}{C_{A0}} = \frac{k \tau}{1 + k \tau} \quad \ll \text{essentially irreversible 1st-order reaction in steady-state CSTR}$$

For a reversible reaction,

$$X_A = \frac{k_f \tau}{1 + (k_f + k_b) \tau} \quad \ll \text{reversible 1st-order reaction in steady-state CSTR}$$

Here is the energy balance again, now combined with our result from the component balance for a single reaction.

$$-(UA T_j + \rho C_{pm} v T_0) + (UA + \rho C_{pm} v) T = (-\Delta H_{rxn}) F_{A0} X_A$$

We can represent this as two energy rate (power) terms that must be equal at steady state.

$$Q_{\text{removal}} = Q_{\text{generation}}$$

$$Q_{\text{removal}} \text{ (J/s)} = -(UA T_j + \rho C_{pm} v T_0) + (UA + \rho C_{pm} v) T$$

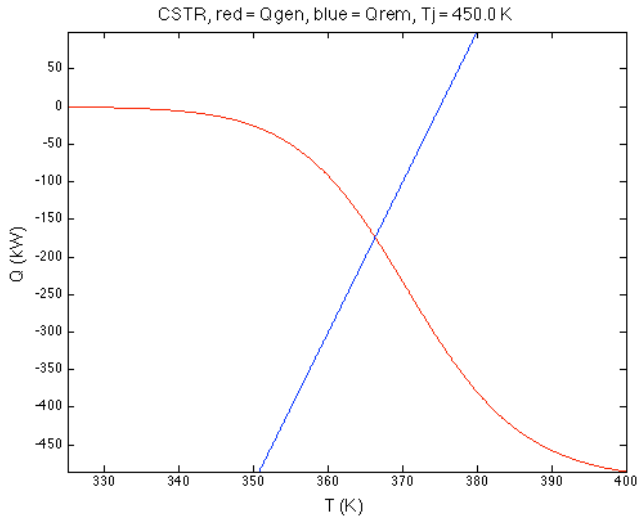
$$Q_{\text{generation}} \text{ (J/s)} = (-\Delta H_{rxn})(-r_A)V = \text{at steady state } (-\Delta H_{rxn}) F_{A0} X_A$$

$Q_{rem}$  is linear in reactor  $T$ , therefore it is a straight line on a  $Q$  vs.  $T$  plot for our case of constant physical properties.  $Q_{rem}$  is positive at higher  $T$  (net energy is removed from the reaction), and has a negative value at lower  $T$  (net energy is supplied to the reaction).

$Q_{gen}$  is nonlinear in reactor  $T$ , through the dependence of rate on the rate coefficients and the exponential dependence of the rate coefficients on  $T$ .

For an endothermic reaction,  $Q_{gen}$  is negative. The intersection of  $Q_{rem}$  and  $Q_{gen}$  is at negative values of  $Q$  on a  $Q$  vs.  $T$  plot.

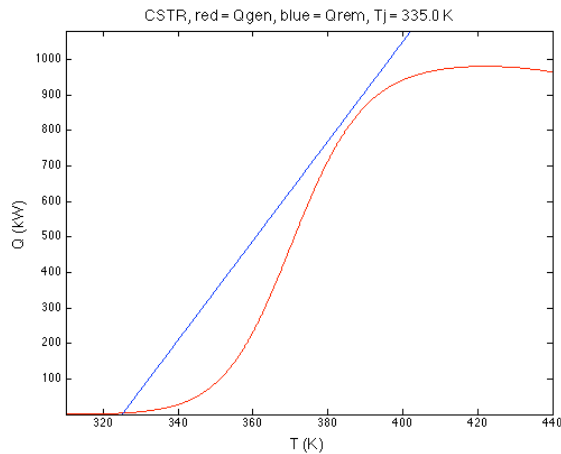
Below is an example of an endothermic reaction in a CSTR. You can see from the shapes of the lines that will be only one steady-state possible for any combination of input values. ***The Matlab scripts used to generate the plots in this document are listed at the end of this document.***



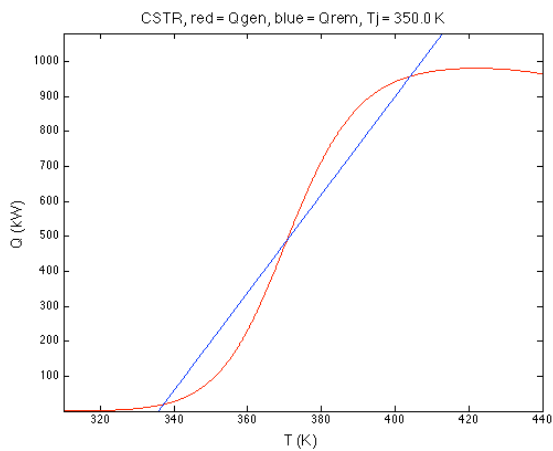
Solution at  $T = 366$  K,  $Q = -174$  kW,  $X_A = 0.348$

For an exothermic reaction,  $Q_{gen}$  is positive. The intersection of  $Q_{rem}$  and  $Q_{gen}$  is at positive values of  $Q$  on a  $Q$  vs.  $T$  plot. Because of the nonlinear shape of  $Q_{gen}$ , which is positive, with respect to the positive slope of  $Q_{rem}$  there can be two stable solutions (two values of  $X_A$  and  $T$ ) for the same input conditions.

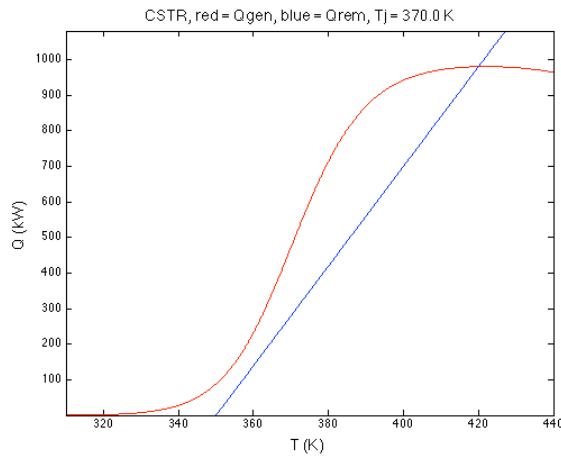
Here is an example of an exothermic reaction in a CSTR with three different heat transfer jacket  $T_j$ 's.



$T_j = 335$  K  
Solution at  $T = 328$  K,  $Q = 4.2$  kW,  $X_A = 0.004$



$T_j = 350$  K  
Solution at  $T = 337$  K,  $Q = 20$  kW,  $X_A = 0.02$  (stable)  
Solution at  $T = 370$  K,  $Q = 488$  kW,  $X_A = 0.49$  (unstable)  
Solution at  $T = 404$  K,  $Q = 957$  kW,  $X_A = 0.96$  (stable)



$T_j = 370 \text{ K}$   
 Solution at  $T = 420 \text{ K}$ ,  $Q = 980 \text{ kW}$ ,  $X_A = 0.98$

The  $Q_{gen}$  curve decreases in magnitude above 420 K because the conversion approaches the equilibrium conversion and the equilibrium conversion decreases with increasing  $T$ .

In the middle plot above, at  $T_j = 350 \text{ K}$ , there are three solutions for  $T$  and  $X_A$ . This property of "multiple steady states" doesn't happen for all exothermic reactions. This would occur for highly exothermic reactions with large activation energies and CSTRs with large heat transfer capacity. While this behavior may be somewhat uncommon, it is very interesting and you should be aware of the possibility of this happening. Why? because small changes in a parameter such as  $T_j$  can lead to abrupt and large changes in reactor  $T$ , as we will see below. Don't be caught off guard.

The middle steady state is unstable to infinitely small perturbations. And reaching it would require a series of unusual operating conditions. Let's say you get your reactor there. Then, in a "thought experiment," say you drop a small, hot, inert rock into the reactor. Your system will move from the middle steady state to the right a small distance. The new point of the system on the  $Q_{gen}$  curve is higher than the new point on the  $Q_{rem}$  line. Therefore, the reactor will heat up and go to the upper steady state at higher  $T$ . If you dropped in a small cold rock, the reactor would go to the lower steady state. Thus, the middle state is an "unstable steady state."

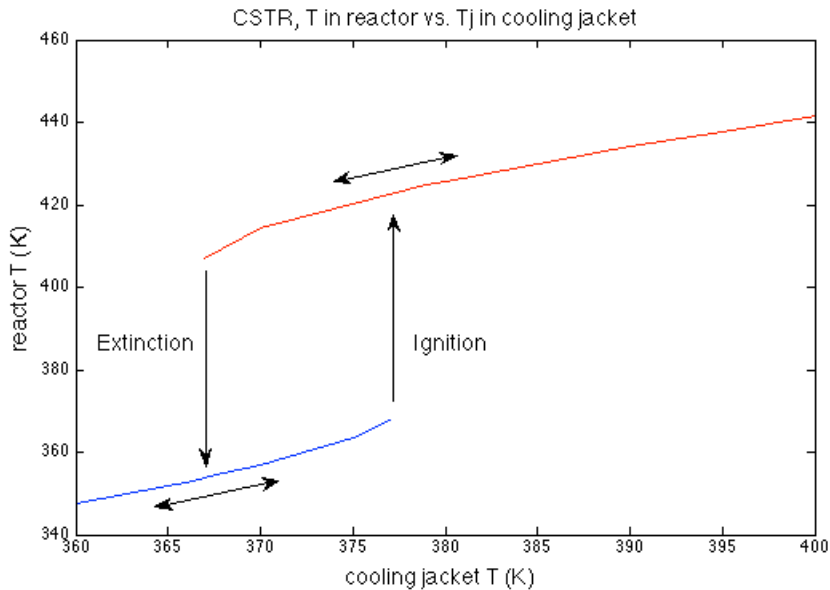
By similar thought experiments, you can demonstrate to yourself that the upper and lower steady states are stable to small perturbations. They are "stable steady states." (These two states are stable because not only this Q curve "slope" criterion is met but also the "dynamic" criterion for stability is met, as discussed below.)

Multiple steady states can be observed in systems with at least two coupled processes, where at least one of the processes is nonlinear. Here, two processes are heat removal, which is linear in  $T$  in our case with constant properties, and heat generation by reaction, which is nonlinear in  $T$ .

Question for you: For a given  $Q_{rem}$  line, what would change in the  $Q_{gen}$  curve between a case where no multiple steady states are possible (lazy S shape) to a case where rate multiplicity is possible (sharp S shape)?

Question for you: For the  $Q_{gen}$  curve where rate multiplicity is possible, what parameter(s) could you change to change the  $Q_{rem}$  line such that no rate multiplicity is possible?

Below is a plot of the steady-state reactor temperature as one of the input parameter values -  $T_j$  in this case - is changed for an exothermic reaction. Very interesting behavior is observed!



Between the "ignition" and "extinction" transitions at  $T_j = 377$  and  $T_j = 366$  K, respectively, is the region of multiple steady states. On the blue "lower branch," you can reversibly change  $T_j$  and get to a predictable  $T$ , thus, the double-headed arrow below the blue curve. On the red "upper branch," you can also reversibly change  $T_j$ .

At the ignition transition, you can jump up 56 K from the low branch to the high branch but you can not jump down. At the extinction transition, you can jump down 54 K from the high branch to the low branch but you can not jump up.

This non reversible behavior at the transitions result in "hysteresis" and a "hysteresis loop" is shown by the arrows. Ignition and extinction transitions commonly occur in chemical reaction systems involving combustion.

Note that there is no way to reach the middle, unstable steady state that we saw above with  $T_j = 370$  K by simply varying a parameter such as  $T_j$ . Reaching it, if possible, would require a series of very unusual operating conditions.

A mechanical analogy to hysteresis is a common toggle light switch vs. a sliding dimmer switch. The toggle switch position vs. switching force exhibits mechanical hysteresis. The sliding dimmer switch gives a change in light intensity proportional to the sliding force.

## Dynamic CSTR with thermal effects

We need to solve both the dynamic energy balance and component balances. For negligible shaft work,

$$\rho C_{pm} V \frac{dT}{dt} = UA(T_j - T) + \rho C_{pm} v(T_0 - T) + \Delta H_{rxn} r_A V$$

$$\frac{dN_A}{dt} = F_{A0} - F_A + r_A V$$

For constant volume of reactor contents,  $V$ , and equal inlet and outlet volumetric flow rates,  $v$ ,

$$V \frac{dC_A}{dt} = v(C_{A0} - C_A) + r_A V$$

The balances can also be expressed as

$$\rho C_{pm} V \frac{dT}{dt} = Q_{gen} - Q_{rem}$$

$$V \frac{dC_A}{dt} = F_{supply} - F_{rxn}$$

For a first-order, essentially irreversible reaction,

$$r_A = -k C_A \quad \text{where} \quad k = A e^{-E_a/(RT)} \quad \text{or} \quad k = k_{T_{ref}} e^{-(E_a/R)(1/T - 1/T_{ref})}$$

The two ODEs become:

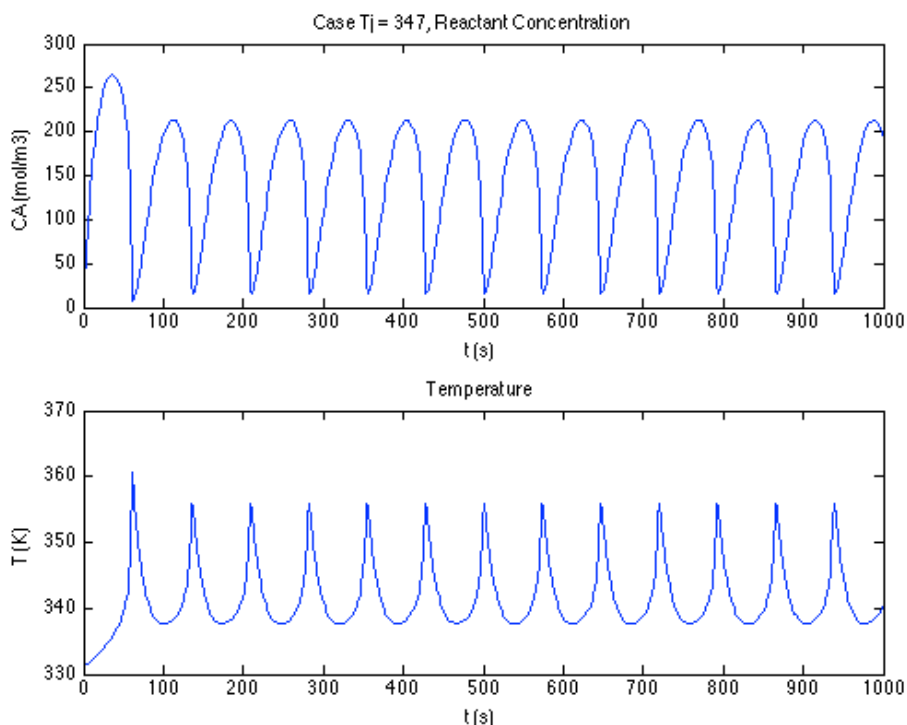
$$\frac{dT}{dt} = \left( \frac{UA}{\rho C_{pm} V} \right) (T_j - T) + \left( \frac{v}{V} \right) (T_0 - T) - \left( \frac{\Delta H_{rxn}}{\rho C_{pm}} \right) k_{T_{ref}} e^{-(E_a/R)(1/T - 1/T_{ref})} C_A$$

$$\frac{dC_A}{dt} = \left( \frac{v}{V} \right) (C_{A0} - C_A) - k_{T_{ref}} e^{-(E_a/R)(1/T - 1/T_{ref})} C_A$$

The two ODEs are coupled because they both depend on reactor temperature and reactant concentration. Below are results we get for integration of the two equations for an interesting case.

$k_{T_{ref}} = k_{300} = 5.0e-06 \text{ s}^{-1}$	$T_j = 347 \text{ K}$
$E_a = 200 \text{ kJ/mol}$	$UA = 20 \text{ kJ/s/K}$
$\Delta H = -250 \text{ kJ/mol}$	$\rho = 1000 \text{ kg/m}^3$
$T_0 = 300 \text{ K}$	$C_{pm} = 2 \text{ kJ/kg/K}$
$C_{A0} = 400 \text{ mol/m}^3$	$V = 0.10 \text{ m}^3$
	$v = 5.0e-3 \text{ m}^3/\text{s}$

At the initial conditions, there is zero concentration of reactant in the reactor and inlet flow, and the contents are at the temperature that would be obtained in the absence of reaction. Then the inlet concentration changes from zero to  $C_{A0}$ .



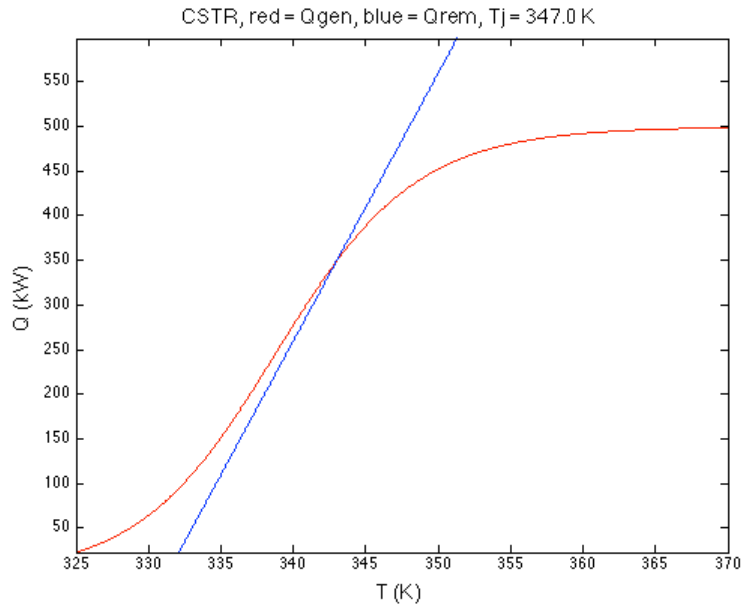
The conditions in the reactor oscillate even though all the input parameters remain constant! The conditions vary periodically in time about a steady state solution in a "limit cycle." The default conditions in ReactorLab's Division Lab 4 Dynamic CSTR have these input values and exhibit these oscillations.

The UA value used for this case is a relatively large heat transfer requirement. The reactor would probably have to consist of a plate heat exchanger and a recirculation pump. The activation energy and the heat of reaction are also very large for this case. Look at the system equations and see how the value of UA could be scaled back and still maintain oscillations. One change that would work: reduce UA, the flow rate, and the rate constant value at 300 K each by the same factor. Similar oscillations will occur but with a longer period.

Oscillations can result when two or more processes are coupled together with each other. There are other cases where oscillations occur. Think oscillating - beating - cells in your heart, which oscillate via a different mechanism.

In the CSTR system, one process is heat removal by fluid flow and heat transfer, a process that is linear in reactor temperature. Another process is heat generation by the exothermic reaction, a process that is nonlinear in reactor temperature through the Arrhenius temperature-dependence of the rate coefficient. A third process is consumption of reactant by reaction, which tends to lower the reaction rate and, thus, tends to lower the heat generation rate. And a fourth process is supply of reactant to the reactor with the feed stream. During oscillations, heat removal and reactant consumption can be considered to act as "restoring forces" to heat generation and temperature increase.

Here is the Q vs. T plot for this case. You can't see from this plot that the steady-state is oscillatory. In fact, steady state was specified in order to produce this plot. Note, however, that the slopes of the two lines at the intersection point do not differ greatly.



Summarize the dynamic energy balance this way:

$$\frac{dH}{dt} = Q_{\text{gen}} - Q_{\text{rem}} \quad (\text{kW}) \quad \text{rate of change of enthalpy in the reactor}$$

$$Q_{\text{gen}} \text{ (kW)} = (-\Delta H_{\text{rxn}})(-r_A)V$$

$$Q_{\text{rem}} \text{ (kW)} = -(UA T_j + \rho C_{pm} v T_0) + (UA + \rho C_{pm} v) T$$

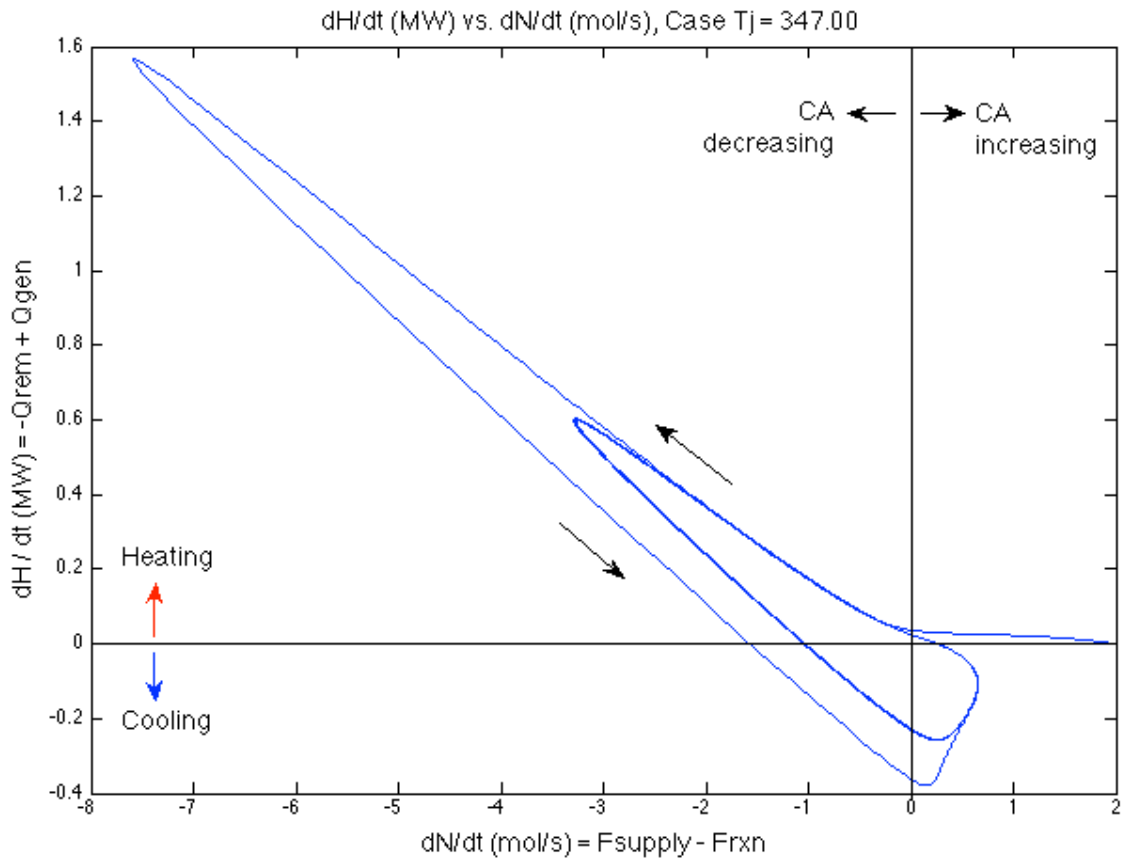
Summarize the dynamic material balance in this way.

$$\frac{dN}{dt} = F_{\text{supply}} - F_{\text{rxn}} = [v(C_{A0} - C_A)] - [k C_A V] \quad (\text{mol/s}) \quad \text{rate of change of moles A in reactor}$$

Continued next page...



By plotting the dynamic energy balance vs. the dynamic material balance ( $dH/dt$  vs.  $dN/dt$ ) we can see better what is happening. The initial condition is at  $dH/dt = 0$  kW and  $dN/dt = 2$  mol/s.



For the reactor to reach steady state,  $dH/dt$  and  $dN/dt$  must both equal zero at the same time. However, for this case, the system "phase curve" periodically moves around that point, which is where the axes cross, in a "limit cycle."

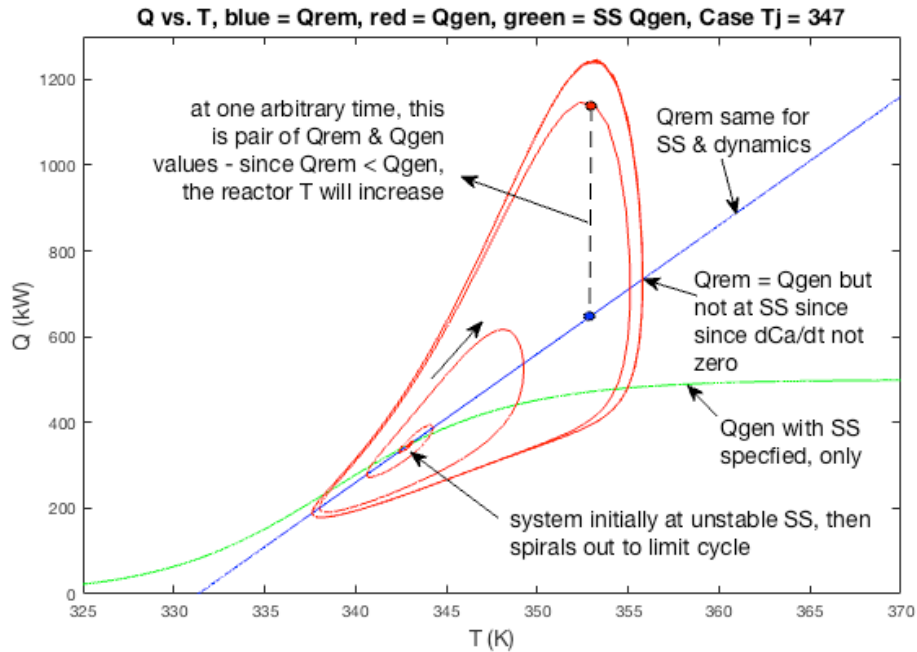
When the reactor is in energy balance at  $dH/dt = 0$  along the horizontal axis and  $Q_{gen} = Q_{rem}$ , it is not in material balance, since  $dN/dt \neq 0$  and  $F_{supply} \neq F_{rxn}$ . Thus, the reactor continues past  $dH/dt = 0$ .

When the reactor is in material balance at  $dN/dt = 0$  along the vertical axis and  $F_{supply} = F_{rxn}$ , it is not in energy balance, since  $dH/dt \neq 0$  and  $Q_{gen} \neq Q_{rem}$ . Thus, the reactor continues past  $dN/dt = 0$ .

The maxima and minima in the  $C_A$  vs. time plot above lie on the vertical axis, where  $dN/dt = 0$ . The maxima and minima in the  $T$  vs. time plot above lie on the horizontal axis, where  $dH/dt = 0$ .

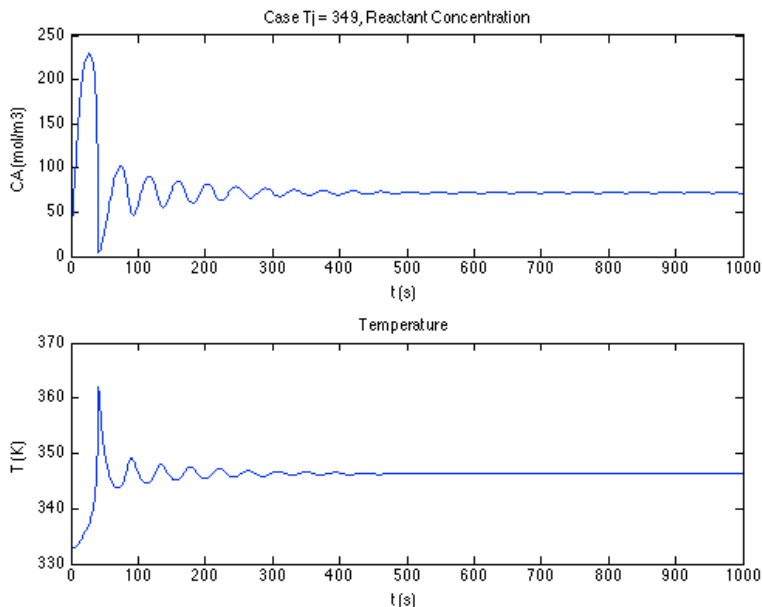
Question for you: Time is implicit in the phase curve plot. Pick a couple distinctive points on the  $C_A$  vs. time and  $T$  vs. time plots, and then locate those and conditions on the phase curve plot.

The Q vs. T plot shown above for this case only applies when steady state is specified. But the system is never at steady state. So does the Q vs. T plot apply at all? Here is the Q vs. T plot for the dynamic system. For this plot, the initial condition is at the (oscillatory) steady-state T and conversion point.

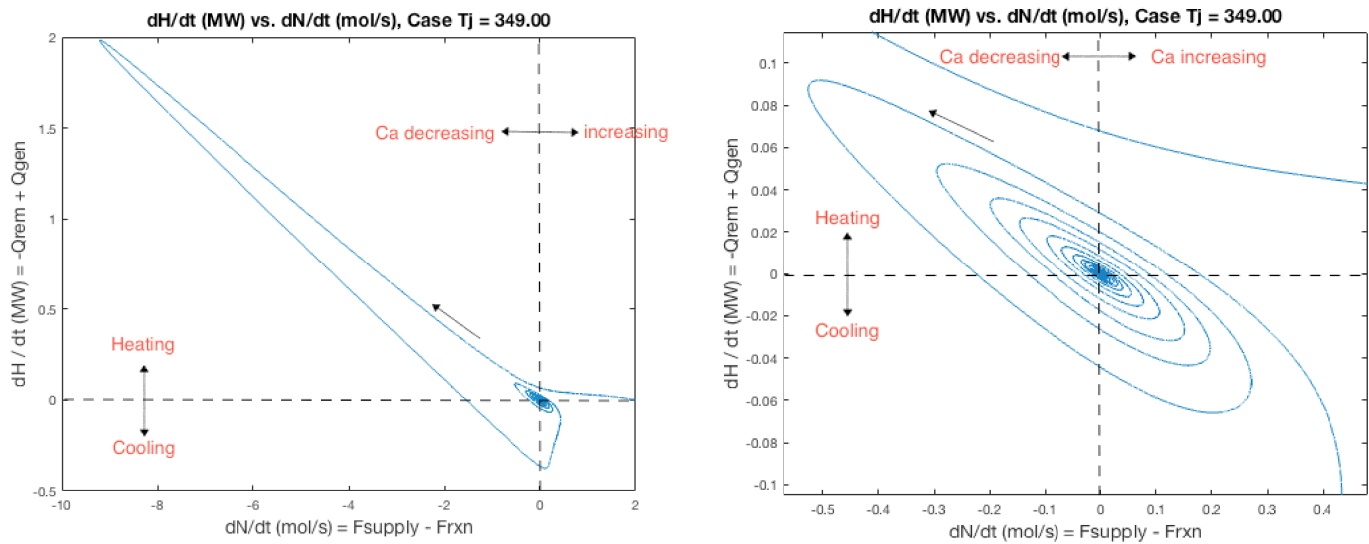


The Qrem line stays the same during dynamics since it is only a function of reactor T and not of reactant concentration. On the other hand, the Qgen curve isn't the same because it also depends on concentration, which is not shown on the plot. In fact there is no fixed Qgen curve during dynamics. The steady-state Qgen curve is not only a function of reactor T but also of concentration and, thus, conversion X. The result  $X = k\tau/(1+k\tau)$  used to draw the steady-state Qgen curve is only correct at steady state when  $dN/dt = VdC_A/dt = 0$ , which it is not during dynamic operation.

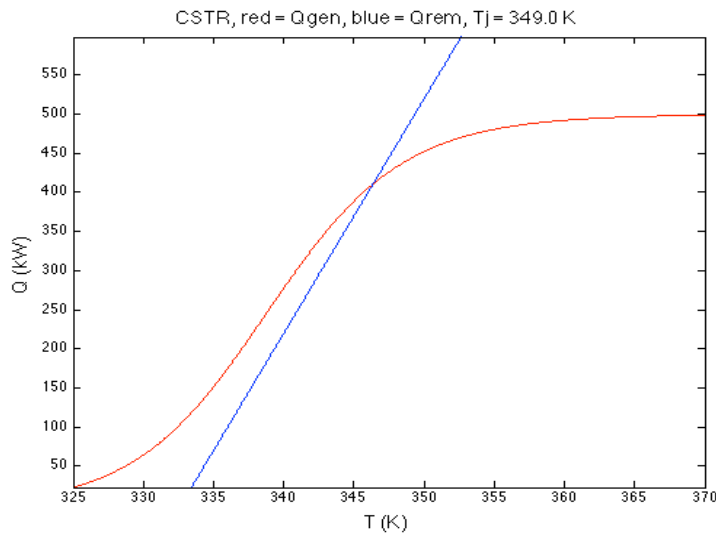
For this CSTR, oscillations occur over a relatively narrow range of conditions. A small change in input parameter can lead to a stable steady state. In the figure below, only the jacket temperature  $T_j$  has been changed.  $T_j$  was changed from 347 K to 349 K.



Here is the  $dH/dt$  vs.  $dN/dt$  plot for this case - zoomed in to show detail on the right.



Here is the steady-state  $Q$  vs.  $T$  plot for this case. Note that the slopes of the two lines at the intersection point differ more in magnitude than the slopes differ in the plot for the first case, where sustained oscillations occur.



### Stability of steady states

Above, we explained the stability and instability of steady states by "thought experiments" in which we dropped a hot or cold rock into the reactor to make a small perturbation.

The stability of steady states in the reactor can be investigated mathematically in at least two ways. One is by doing many numerical simulations. Another way, which may give more insight, is by linearizing the nonlinear energy and material balances around a specified steady-state condition. A linearized model is a good approximation to the original nonlinear model only for small deviations from the specified steady state.

For the linearized system, linear control theory can be used to determine the stability and dynamics of the linearized system about the specified steady state.

During the linearization process, any given nonlinear term is linearized using a first-order Taylor series expansion. Subscript "ss" here means values at the specified steady state. Superscript "Δ" specifies a "deviation variable," which is the deviation of a variable's value from the value at the specified steady state. Here is an example of a nonlinear term  $f(x,y)$  that is a function of two variables,  $x$  and  $y$ .

$$f(x,y) \approx f(x_{ss}, y_{ss}) + \left( \frac{\partial f}{\partial x} \right)_{ss} x^\Delta + \left( \frac{\partial f}{\partial y} \right)_{ss} y^\Delta \quad \text{where} \quad x^\Delta = (x - x_{ss}) ; y^\Delta = (y - y_{ss})$$

In our balance equations, we have this nonlinear term. I will let you linearize it.

$$f(T, C_A) = k C_A = A e^{-E/RT} C_A$$

To linearize the system, substitute the definitions for the deviation variables and the linearized nonlinear terms into the balance equations. Then write a version of the equations with all values at the steady state. Finally, subtract each of the second balance equations (at SS) from the first equation.

Here we also make the time and concentration dimensionless by introducing definitions for dimensionless time and reactant conversion. (hint,  $C/C_0 = (1-X) = 1/(1+k\tau)$ )

One could also make temperature dimensionless, as do Uppal, et al. (1974) [reference below]. We do not do that in order to keep things a little less abstract.

$$t^* = t/\tau ; \tau = V/v \quad \text{dimensionless time}$$

$$X = \frac{C_{A0} - C_A}{C_{A0}} \quad \text{conversion for this constant flow rate system}$$

$$X^\Delta = \frac{-C_A^\Delta}{C_{A0}} ; \frac{dC_A^\Delta}{dt} = -C_{A0} \frac{dX^\Delta}{dt}$$

The result is this system of linear equations.

$$A \vec{y} = \frac{d\vec{y}}{dt^*}$$

$$\begin{bmatrix} -(1+k_{ss}\tau) & \left( \frac{E_a}{R_g T_{ss}^2} \right) X_{ss} \\ -\left( \frac{-\Delta H k_{ss} \tau C_{A0}}{\rho C_{pm}} \right) & \left( -\left( 1 + \frac{UA}{\rho C_{pm} v} \right) + \left( \frac{-\Delta H C_{A0}}{\rho C_{pm}} \right) \left( \frac{E_a}{R_g T_{ss}^2} \right) X_{ss} \right) \end{bmatrix} \begin{bmatrix} X^\Delta \\ T^\Delta \end{bmatrix} = \begin{bmatrix} \frac{dX^\Delta}{dt^*} \\ \frac{dT^\Delta}{dt^*} \end{bmatrix}$$

The characteristic equation of the linearized system is

$$\lambda^2 + (-\text{tr } \mathbf{A})\lambda + (\det \mathbf{A}) = 0$$

$$\lambda^2 + a_1\lambda + a_0 = 0$$

where "tr" is the matrix trace and "det" is the matrix determinant.

This is equation 18 in Uppal, et al. (1974). Also refer to your process control course notes for a multiple input system.

The equations given in Uppal's paper look more complex than those above because the  $T_{ss}$  terms in Uppal are replaced by  $T_{ss} = f(X_{ss})$  to get complex equations in  $X_{ss}$ . This allows them to specify an  $X_{ss}$  value and directly compute how the change in a parameter value such as UA affects the roots.

The coefficients are as follows. Note changing a parameter value such as UA will also change the values of both  $T_{ss}$  and  $X_{ss}$ .

$$a_1 = (-\text{tr } \mathbf{A}) = \left(1 + k_{ss} \tau\right) + \left(1 + \frac{UA}{\rho C_{pm} v}\right) - \left(\frac{-\Delta H C_{A0}}{\rho C_{pm}}\right) \left(\frac{E_a}{R_g T_{ss}^2}\right) X_{ss}$$

$$a_0 = (\det \mathbf{A}) = \left(1 + k_{ss} \tau\right) \left(1 + \frac{UA}{\rho C_{pm} v}\right) - \left(\frac{-\Delta H C_{A0}}{\rho C_{pm}}\right) \left(\frac{E_a}{R_g T_{ss}^2}\right) X_{ss}$$

For this second-order polynomial equation, the roots are given by the quadratic formula.

$$\lambda = \frac{-a_1 \pm \sqrt{a_1^2 - 4a_0}}{2}$$

These roots are the eigenvalues of the system. Components of the dynamic response consist of exponential terms whose exponents are the real parts of the roots multiplied by dimensionless time. These dynamic deviation variable terms will decay to zero (zero deviation) when the real parts of the roots are negative.

When complex conjugate roots are present (term in square root is negative), sine wave terms will be present with a frequency equal to the complex part of the roots.

There are three groups of terms that determine the roots.

$$a_1 = R + H - G \quad \text{and} \quad a_0 = R H - G$$

where

$$R = (1 + k_{ss} \tau) = 1 / (1 - X_{ss}) = C_{A0} / C_{A,ss} \quad \text{Reaction term}$$

$$H = \left( 1 + \frac{UA}{\rho C_{pm} v} \right) = \left( \frac{1}{\rho C_{pm} v} \right) \frac{dQ_{rem}}{dT} \quad \text{Heat transfer term}$$

$$G = \left( \frac{-\Delta H C_{A0}}{\rho C_{pm}} \right) \left( \frac{E_a}{R_g T_{ss}^2} \right) X_{ss} = \left( \frac{R}{\rho C_{pm} v} \right) \frac{dQ_{gen}}{dT} \quad \text{Generation term}$$

There are limits to these terms.  $R > 1$  when reaction occurs.  $H = 1$  for an adiabatic reactor.  $H > 1$  for a non-adiabatic reactor.  $G > 0$  for an exothermic reaction.

Uppal et al. (1974) states that the necessary and sufficient condition for stability of a steady state is  $a_1 > 0$  and  $a_0 > 0$ . A footnote says that roots with a zero real part "must be treated by other methods."

The criterion  $a_0 > 0$  is called the "slope criterion." It is when the slope of  $Q_{rem} > \text{slope } Q_{gen}$ . The system is stable in the "hot rock" thought experiment above.

$$a_0 = R H - G > 0$$

$$R H > G$$

$$R \left( \frac{1}{\rho C_{pm} v} \right) \frac{dQ_{rem}}{dT} > \left( \frac{R}{\rho C_{pm} v} \right) \frac{dQ_{gen}}{dT}$$

$$\frac{dQ_{rem}}{dT} > \frac{dQ_{gen}}{dT}$$

The criterion  $a_1 > 0$  is called the "dynamic criterion" and it also has to be met for stability. A steady state will be unstable when the dynamic criterion is not met, even though the slope criterion is met. This can be confirmed by solution of the nonlinear differential equations. See Uppal's paper for many cases, including those in which the high state in a multiple steady state solution obeys the slope criterion ("hot rock" experiment) but not the dynamic criterion and, so, is unstable.

For  $(a_1^2 - 4a_0) \geq 0$  the roots of the characteristic equation are real, and the response is not oscillatory. When both roots are negative, a damped response back to the steady state is obtained after a perturbation, i.e., the steady state is stable to small perturbations. If one or both roots are positive, the system will diverge from the steady state after a perturbation, i.e., the steady state is unstable.

For  $(a_1^2 - 4a_0) < 0$  the roots of the characteristic equation are a complex conjugate pair, and the response is oscillatory. When  $a_1 > 0$  the real part of the root is negative and a damped oscillatory response back to the steady state is obtained after a perturbation. This type of response is shown by the plots for the original nonlinear system at  $T_j = 349$  K. When  $a_1 < 0$  the real part of the root is positive and the system will diverge from the steady state after a perturbation.

For a damped response in this linearized system,

$$a_1 = R + H - G > 0$$

$$R + H > G$$

$$\frac{dQ_{rem}}{dT} > R \left( \frac{dQ_{gen}}{dT} - \rho C_{pm} v \right)$$

So  $a_0 > 0$  means the slope of  $Q_{rem}$  must be greater than the slope of  $Q_{gen}$ , and  $a_1 > 0$  means the slope of the  $Q_{rem}$  line must, in addition, be greater than the slope of  $Q_{gen}$  by some factor to get a stable, damped response. Damping requires that heat removal is significantly more sensitive to changes in reactor temperature than is heat generation.

Remember the  $Q$  vs.  $T$  plots above for the sustained oscillatory and damped oscillatory responses in the original nonlinear system. The slope of  $Q_{rem}$  was noticeably greater than the slope of  $Q_{gen}$  for the damped nonlinear case than it was in the oscillatory nonlinear case.

For the linearized damped oscillatory case,  $dQ_{rem}/dT = 30$  kW/K and  $dQ_{gen}/dT = 14.7$  kW/K, a difference of 15.3 kW/K.

For the linearized sustained oscillatory case,  $dQ_{rem}/dT = 30$  kW/K and  $dQ_{gen}/dT = 22.1$  kW/K, a difference of 7.9 kW/K.

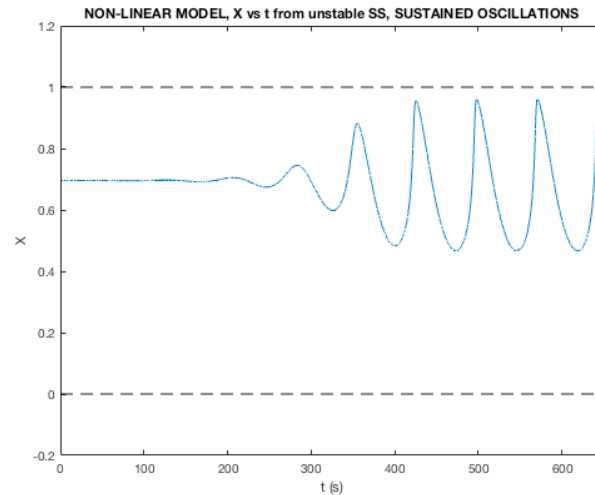
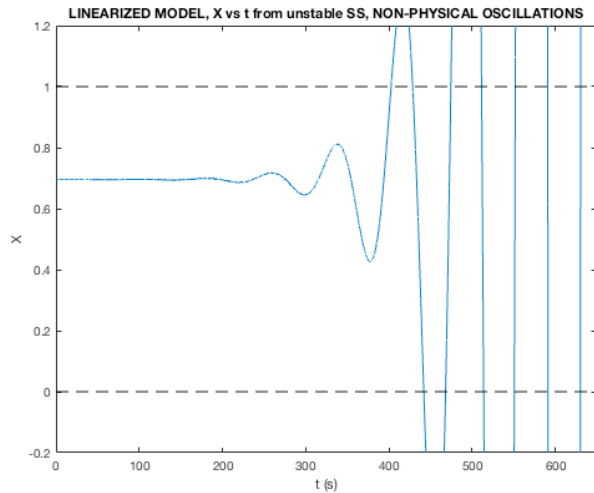
For  $(a_1^2 - 4a_0) < 0$  and  $a_1 = 0$  such that the real part of the complex root is zero valued, the linearized system will exhibit sustained oscillations in a "limit cycle" about the steady state.

Remember that the characteristic equation's root conditions are for a linear system, whereas the real reactor is a nonlinear system. For the linearized system, the variables  $T$  and  $X$  can diverge from the steady state by unlimited amounts. However, a linearized model is a good approximation only for small deviations from the specified steady state.

In the real nonlinear system,  $X$  is constrained between limits,  $0 < X < 1$ , and  $T$  is also constrained by the operating conditions.

Because of these constraints, a set of operating conditions in the linearized system that results in an unstable oscillatory response, can result in sustained oscillations in the nonlinear system.

This is shown below for  $T_j = 347$  K.



Question for you: What are the values of the roots for the examples discussed above?

Question for you: There are three groups of terms in the coefficients that determine the roots: R, H, G. What are the relative values of the terms that result in different types of characteristic responses (decay, growth, oscillation)? State your answers in qualitative terms, e.g., "high heat of reaction," or "low activation energy."

Question for you: Can an adiabatic reactor exhibit oscillations?

The linearized model shows that oscillations can be obtained even when two linear systems couple (linearized material balance and energy balance, two ODEs).

The original CSTR system also has two systems coupled together but at least one is nonlinear.

There are also isothermal chemical systems that can oscillate. Biomass growth and substrate feed and consumption in a bioreactor is an example. The Belousov-Zhabotinsky reaction system is another. These examples have competing, coupled nonlinear processes which can produce oscillations.

## SUMMARY

Endothermic reactions in CSTRs have one steady state, which is stable.

Exothermic reactions in CSTRs with heat transfer can have one steady state, or multiple steady states: two stable steady states and one unstable steady state.

In addition, exothermic reactions in CSTRs with heat transfer can exhibit oscillations under some operating conditions with steady inputs.



The oscillations are due to the coupling between heat transfer and heat generation by reaction. Steady states are stable when the slope of the heat removal line is greater than the slope of the heat generation curve at their intersection.

When the slopes of these lines differ to a relatively small extent, then sustained oscillations can result. The oscillations are produced by the coupling between heat transfer and heat generation. The oscillation amplitudes are bounded because of the constraints on supply and conversion of reactant, and can continue indefinitely.

When the slopes of the heat removal line is significantly greater than the slope of the heat generation curve at their intersection, there will be a damped response to perturbations, possibly oscillatory, and the system will settle back to the steady state.

### Vocabulary

steady state

- stable

- unstable

- oscillatory

exothermic

endothermic

sign (positive, negative) of heat of reaction for endothermic, exothermic

$Q_{rem}$ , heat removal line

$Q_{gen}$ , heat generation curve

multiple steady states

hysteresis loop

- low branch, high branch

- ignition, extinction

oscillation

- damped, sustained

perturbation

phase curve

limit cycle

restoring force

linearization

first-order Taylor series expansion

deviation variable

slope criterion for stability

dynamic criterion for stability

characteristic equation of linear system

eigenvalue

complex conjugate roots (of polynomial)

## Simulations in ReactorLab - CSTRs

See <http://www.ReactorLab.net>  
Division 3 Thermal Effects  
Lab 3 Steady State CSTR  
Lab 4 Dynamic CSTR

## Additional Resources

For information about the amazing multiple steady states and dynamics of CSTRs, see the theoretical papers listed below:

Uppal, A., Ray, W.H., and Poore, A.B., "On the dynamic behavior of continuous stirred tank reactors," *Chem. Eng. Sci.*, vol. 29, pp. 967-985 (1974).  
<http://www.sciencedirect.com/science/article/pii/0009250974800898>

Uppal, A., Ray, W.H., and Poore, A.B., "The classification of the dynamic behavior of continuous stirred tank reactors - influence of reactor residence time," *Chem. Eng. Sci.*, vol. 31, pp. 205-214 (1976).  
<http://www.sciencedirect.com/science/article/pii/0009250976850580>

For analysis of experimental data from industrial reactors that exhibited oscillations, see

Vleeschhouwer, P.H.M., Garton, R.D., and Fortuin, J.M.H., "Analysis of limit cycles in an industrial oxo reactor," *Chem. Eng. Sci.*, vol. 47, pp. 2547-2552 (1992).  
<http://www.sciencedirect.com/science/article/pii/0009250992870914>

Jesus, N.J.C., Melo, P.A., Nele, M. and Pinto, J.C., "Oscillatory behaviour of an industrial slurry polyethylene reactor," *Canadian J. Chem. Eng.*, vol. 89, no. 3, pp. 582-592 (2011).  
<http://onlinelibrary.wiley.com/doi/10.1002/cjce.20444/abstract>

## Matlab script for ENDOthermic CSTR

```
% ENDOTHERMIC steady-state CSTR energy balance
clear
Ef = 150; % kJ/mol, activation energy
Eb = 100; % kJ/mol, activation energy
DH = Ef-Eb; % kJ/mol, heat of reaction
kf300 = 1e-6; % (1/s)
kb300 = 1e-12; % = 0 for essentially irreversible
rho = 0.5e3; % kg/m3, fluid density
Cpm = 2; % kJ/kg, fluid heat capacity
UA = 10; % kJ/s/K
V = 0.1; % m3, fluid volume in CSTR
v = 1e-2; % m3/s, fluid flow rate
To = 300; % K, inlet fluid T
Tj = 450; % K, heat transfer jacket T
Cao = 1e3; % mol/m3, inlet concentration of reactant A
Rg = 8.3145e-3; % gas constant, kJ/mol/K
tau = V/v; % sec, space time
```

```

T = linspace(325,400,1000); % K, reactor T array
kf = kf300*exp(-(Ef/Rg)*(1./T - 1/300)); % kf(T) is an array
kb = kb300*exp(-(Eb/Rg)*(1./T - 1/300)); % kb(T) is an array
X = kf*tau ./ (1+(kf+kb)*tau); % X(T), conversion of A is an array

Qgen = -DH * v * Cao * X; % Qgen(T) is an array
Qrem = -(UA*Tj + rho*Cpm*v*To) + (UA + rho*Cpm*v)*T; % Qrem(T) is an array

plot(T,Qgen,'r',T,Qrem,'b')
axis([min(T) max(T) min(Qgen) max(Qgen)+100])
tt = sprintf('CSTR, red = Qgen, blue = Qrem, Tj = %3.1f K',Tj)
title(tt,'FontSize',14)
ylabel('Q (kW)','FontSize',14)
xlabel('T (K)','FontSize',14)

% find T's at solutions
cc = 1; % convergence criterion, may have to adjust
[rows cols vals] = find(abs(Qgen-Qrem)<cc);
Tss = T(cols), Qss = Qgen(cols), Xss = Qss/(-DH*v*Cao)

```

### Matlab script for EXOthermic CSTR

This is the same program, just different parameter values. I show both to prevent mixing up which parameter value set was used for which plot.

```

% EXOTHERMIC steady-state CSTR energy balance
clear
Ef = 120; % kJ/mol, activation energy
Eb = 220; % kJ/mol, activation energy
DH = Ef-Eb; % kJ/mol, heat of reaction
kf300 = 1e-5; % (1/s)
kb300 = 1e-12; % = 0 for essentially irreversible
rho = 0.4e3; % kg/m3, fluid density
Cpm = 1; % kJ/kg/K, fluid heat capacity
UA = 10; % kJ/s/K
V = 0.1; % m3, fluid volume in CSTR
v = 1e-2; % m3/s, fluid flow rate
To = 300; % K, inlet fluid T
Tj = 350; % K, heat transfer jacket T
Cao = 1e3; % mol/m3, inlet concentration of reactant A
Rg = 8.3145e-3; % gas constant, kJ/mol/K
tau = V/v; % sec, space time

T = linspace(310,440,1000); % K, reactor T array
kf = kf300*exp(-(Ef/Rg)*(1./T - 1/300)); % kf(T) is an array
kb = kb300*exp(-(Eb/Rg)*(1./T - 1/300)); % kb(T) is an array
X = kf*tau ./ (1+(kf+kb)*tau); % X(T), conversion of A is an array

Qgen = -DH * v * Cao * X; % Qgen(T) is an array
Qrem = -(UA*Tj + rho*Cpm*v*To) + (UA + rho*Cpm*v)*T; % Qrem(T) is an array

plot(T,Qgen,'r',T,Qrem,'b')
axis([min(T) max(T) min(Qgen) max(Qgen)+100])
tt = sprintf('CSTR, red = Qgen, blue = Qrem, Tj = %3.1f K',Tj);
title(tt,'FontSize',14)
ylabel('Q (kW)','FontSize',14)
xlabel('T (K)','FontSize',14)

% find T's at solutions
cc = 1; % convergence criterion, may have to adjust
[rows cols vals] = find(abs(Qgen-Qrem)<cc);
Tss = T(cols), Qss = Qgen(cols), Xss = Qss/(-DH*v*Cao)

```

## Matlab script for Dynamic CSTR - MAIN script - see function script below

```
% First-order, essentially irreversible reaction in a CSTR
% with heat transfer

close all
clear all

global vol sv k300 Ea Rg Tin Tj UA rvc H dens capac cin

k300 = 5.0E-6; % (1/s), rate coefficient value at 300 K
Ea = 200; % (kJ/mol), activation energy
H = -250; % (kJ/mol), heat of reaction, negative is exothermic
Tin = 300; % (K), inlet reactant T
cin = 400; % (mol/m3), inlet reactant concentration
flow = 5.0e-03; % (m3/s), flow rate of reactants in and out of reactor
Tj = 347; % (K), jacket T
UA = 20; % (kJ/(s K)), heat transfer coefficient times area
dens = 1000; % (kg/m3), density of liquid contents of reactor
capac = 2; % (kJ/(kg K)), heat capacity of reactor contents
vol = 0.1; % (m3), volume of reactor contents
Rg = 0.00831446; % (kJ/(mol K))

sv = flow/vol; % space velocity
rvc = dens * vol * capac;

intercept = (dens*flow*capac*Tin+UA*Tj); % (kJ)
slope = (dens*flow*capac+UA); % (kJ/K)
Tnorxn = intercept/slope; % T if no reaction (K)

% set time span over which to integrate
% add more points to get better resolution near Qgen = Qrem
tSpan = linspace(0,1000,20000); % [0 1000];
y0 = [0,Tnorxn]; % set initial cond. at t = 0

% call ode45 integrator
% 'cstrD' is defined in the file "cstrD.m" that contains the derivatives
[t,y] = ode45('cstrD', tSpan, y0);

conc = y(:,1);
Tr = y(:,2);

tt = sprintf('Reactant Concentration, Case Tj = %6.2f',Tj)
subplot(2,1,1), plot(t,conc), title(tt,'FontSize',14),
    ylabel('CA (mol/m3)','FontSize',14), xlabel('t (s)','FontSize',14)
subplot(2,1,2), plot(t,Tr), title('Temperature','FontSize',14),
    ylabel('T (K)','FontSize',14), xlabel('t (s)','FontSize',14)

% now look at Qremoval & Qgeneration
% for both steady and unsteady state: Qgen = -H*(-rA)*vol
% this is true at steady state only: Qgen = -H*fA0*x = -H*flow*cin*x
% where x = (cin - conc)/cin and tau = vol/flow = 1/sv
% since tau*dx/dt = -x + k*tau*(1-x)
% only at SS: x = k*tau*(1-x)
% so only at SS: flow*cin*x = k*tau*flow*cin*(1-x), which = (-rA)*vol

tfac = (1/300) - (1 ./ Tr);
k = k300 * exp(Ea*tfac/Rg);
Qgen = -H .* k .* conc .* vol; % k and conc are arrays so use dot operator
Qrem = -(UA*Tj+dens*capac*flow*Tin) + (UA+dens*capac*flow)*Tr;
```

```

% at unsteady state
% dens*capac*vol*dTr/dt = -Qrem + Qgen
% so when Qgen > Qrem, T increases

figure(2)
plot(t,Qgen,'r',t,Qrem,'b')
tt = sprintf('red = Qgen, blue = Qrem, Case Tj = %6.2f',Tj)
title(tt,'FontSize',14)
xlabel('t (s)','FontSize',14)
figure(3)
tmax = 1300;
tline = linspace(0,tmax,3000); % for diagonal line & data cursor for SS pt
plot(Qrem,Qgen,'k',tline,tline,'b')
axis([0 tmax 0 tmax])
tt = sprintf('Qgen vs. Qrem (Qrem proportional to reactor T, Case Tj = %6.2f',Tj)
title(tt,'FontSize',14)
ylabel('Qgen (kW)','FontSize',14)
xlabel('Qrem (kW)','FontSize',14)
figure(4)
Fsupply = flow*(cin - conc); % (mol/s) net rate reactant supply by flow
Frnx = k .* conc .* vol; % (mol/s) rate reactant consumption by reaction
plot(Fsupply,Frnx)
axis([0 10 0 10])
tt = sprintf('Frnx (mol/s) vs. Fsupply (mol/s), Case Tj = %6.2f',Tj)
title(tt,'FontSize',14)
ylabel('Frnx (mol/s) = reactant reaction rate','FontSize',14)
xlabel('Fsupply (mol/s) = reactant supply rate to reactor','FontSize',14)
figure(5)
% at a steady state, both rates of change would be zero
dNdt = Fsupply - Frnx; % (mol/s), rate of change of moles A in reactor
dHdt = -Qrem + Qgen; % (kW), rate of change in reactor enthalpy
dHdtMW = dHdt/1000; % (MW)
plot(dNdt,dHdtMW)
tt = sprintf('dH/dt (MW) vs. dN/dt (mol/s), Case Tj = %6.2f',Tj)
title(tt,'FontSize',14)
ylabel('dH / dt (MW) = -Qrem + Qgen','FontSize',14)
xlabel('dN/dt (mol/s) = Fsupply - Frnx','FontSize',14)

```

### Matlab script for Dynamic CSTR - FUNCTION - listing of file cstrD.m

```

function ydot = cstrD(t,y)
% y holds the dependent variables
% y(1) is dependent variable #1, conc, reactant conc in reactor
% y(2) is dependent variable #2, Tr, temperature in reactor
% t is the independent variable, time
% ydot receives the values of the derivatives
% ydot(1) = dy(1)/dtau = dconc/dt
% ydot(2) = dy(2)/dtau = dTr/dt

global vol sv k300 Ea Rg Tin Tj UA rvc H dens capac cin

% initialize ydot vector
ydot = [0;0]; % two zeros because two diff. equations

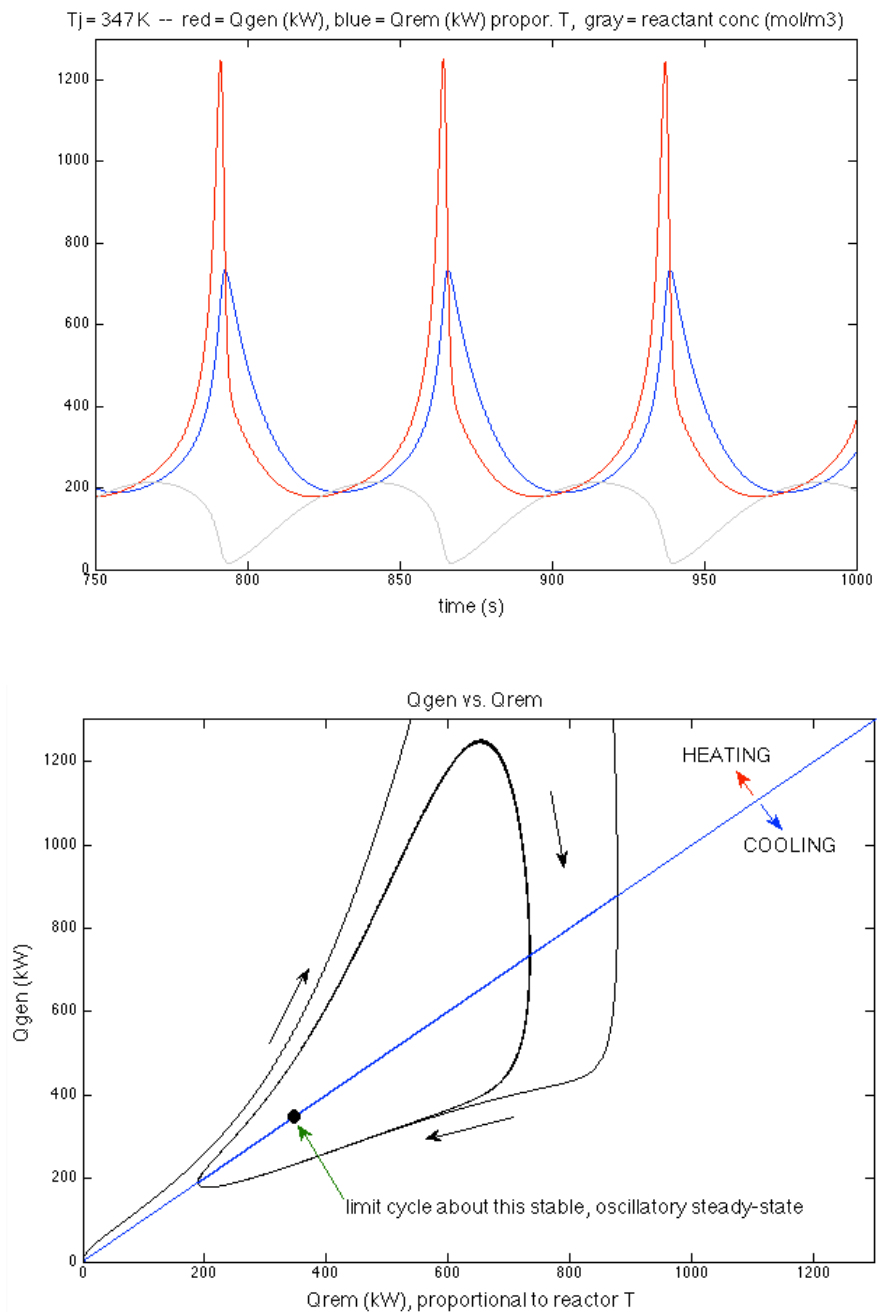
% y(1) and y(2) are both one-element arrays so
% DO NOT need dot operators ( .* ./) here
tfac = (1/300) - (1/y(2));
k = k300 * exp(Ea*tfac/Rg);
K1 = Tin*sv + UA*Tj/rvc;
K2 = sv + UA/rvc;
K3 = H*k/(dens*capac);

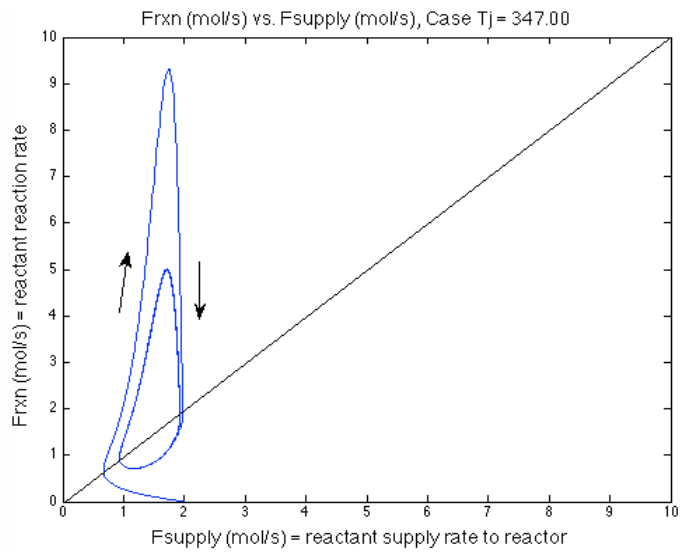
ydot(1) = cin * sv - (k + sv) * y(1);
ydot(2) = K1 - K2 * y(2) - K3 * y(1);

```

## APPENDIX

Below are some plots from earlier versions of these notes. The first three plots below are for the case above with sustained oscillations,  $T_j = 347$  K.





The plot below is for the damped oscillatory case with  $T_j = 349\text{ K}$

