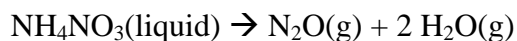


HOMEWORK 6 KEY

Problem 1: Quoting from the Wilmington, DE *Morning News*, Aug. 3, 1977:

“Investigators sift through the debris from blast in quest for the cause [why the new chemical plant exploded]. A company spokesman said it appears... likely that the [fatal] blast was caused by [rapid decomposition of] ... ammonium nitrate [NH₄NO₃] used to produce nitrous oxide [N₂O].”

In the process, a T=200°F aqueous solution, 83 wt% ammonium nitrate, is fed into a CSTR. When the process is running normally at steady state, about 140 kg/hr of the aqueous solution is injected, and the temperature in the reactor, T_R, is 510°F. At this temperature, the water evaporates rapidly, but the molten ammonium nitrate remains in the CSTR, slowly decomposing by this reaction:



$$k(T=510^\circ\text{F}) = 0.307/\text{hour}$$

$$\Delta H_{\text{rxn}}(T=510^\circ\text{F}) = -740 \text{ kJ/kg of ammonium nitrate}$$

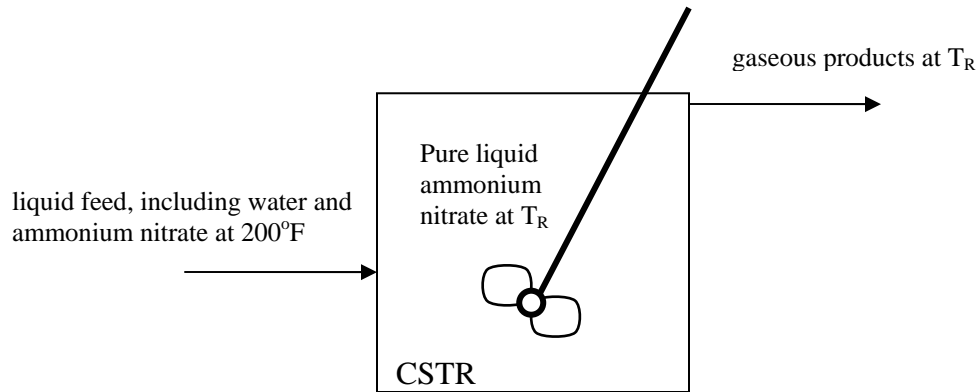
Note that it takes about 2.2 MJ to convert a kg of liquid water at 200°F to a kg of steam at 500°F.

Also, FYI:

$$C_p(\text{steam}) = 2 \text{ kJ/kg-degree F}$$

$$C_p(\text{liquid NH}_4\text{NO}_3) = 0.8 \text{ kJ/kg-degree F}$$

Neglect non-ideal mixing effects and assume that NH₄NO₃ enters as a liquid. Assume that ΔH_{rxn} is approximately constant in the reactor temperature ranges of the problem. A diagram is shown below.



This document will follow these symbolic conventions when multiple interpretations are possible:

An extensive property is given by an underbar

A molar intensive property has no extra notational information

An intensive property that is per unit of mass is given with a carrot

Extents of reaction are in units of moles per time

Also, ideal mixing is assumed.

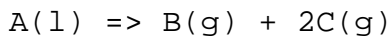
(a) During normal steady-state operation, what mass (kg) of ammonium nitrate resides in the reactor? *Note that there is negligible hold-up of any gases within the reactor.*

Input state: liquid water and liquid ammonium nitrate are fed at 200°F

Reaction State: temperature is T_R , negligible gases are present

Output state: only gases may exit, gases exit at T_R

The components are renamed A, B, and C as in the following:



A = ammonium nitrate

B = N_2O

C = H_2O

First, define extent of reaction ξ in terms of reaction rate:

$$\dot{\xi} = rV = k[A]V = kN_A = (k/MW_A)(N_A MW_A) = (k/MW_A)(m_A)$$

Mole/mass balances on each component in the system yield the following relationships:

Ammonium Nitrate Balance

$$\frac{dm_A}{dt} = \dot{m}_{Ain} - \dot{m}_{Aout} - \dot{\xi} MW_A$$

Apply steady state, no liquid exits:

$$0 = \dot{m}_{Ain} - km_A$$

Equivalent mole balance:

$$0 = F_{Ain} - \dot{\xi}$$

Nitrous oxide mass balance

$$\frac{dm_B}{dt} = \dot{m}_{Bin} - \dot{m}_{Bout} + \dot{\xi} MW_B$$

Apply steady state, nothing enters

$$0 = -\dot{m}_{Bout} + k m_A \frac{MW_B}{MW_A}$$

Equivalent mole balance:

$$0 = -F_{Bout} + \dot{\xi}$$

Water mass balance

$$\frac{dm_C}{dt} = \dot{m}_{Cin} - \dot{m}_{Cout} + 2\dot{\xi} MW_C$$

Apply steady state

$$0 = \dot{m}_{Cin} - \dot{m}_{Cout} + 2k m_A \frac{MW_C}{MW_A}$$

Equivalent mole balance:

$$0 = F_{Cin} - F_{Cout} + 2\dot{\xi}$$

Thus we can express the molar extent of reaction in terms of the molar flow rates:

$$\dot{\xi} = \frac{(F_{Cout} - F_{Cin})}{2} = F_{Ain} = F_{Bout}$$

Part (a) can be answered using the ss. mass balance on component A:

$$0 = \dot{m}_{Ain} - km_A$$

Hence, we can find the holdup of ammonium nitrate in the reactor at 510 Fahrenheit to be:

$$\frac{\dot{m}_{Ain}}{k(510^\circ F)} = m_A = \frac{(0.83)(140 \text{ kg/h})}{0.307 \text{ h}^{-1}} = 378.5 \text{ kg}$$

(b) How much cooling capacity (in kW) is required for this reactor when it is running in steady state? If this is provided by excess cooling water with an average temperature $T_a = 100^\circ \text{F}$, what is the product of the heat transfer coefficient and the area, UA , in kW/F° ?

To answer part (b), we need an enthalpy (energy) balance on the open system.

Enthalpy Balance (assuming negligible gas holdup in reactor), mass and molar formats:

$$\frac{dH}{dt} = \frac{d\left(\sum_i \hat{c}_{p,i} m_i T\right)}{dt} = \frac{d\left(\sum_i c_{p,i} N_i T\right)}{dt} = \frac{d(m_A \hat{c}_{p,A} T)}{dt} = \frac{d(N_A c_{p,A} T)}{dt}$$

$$\frac{dH}{dt} = \sum_i \dot{m}_{i,in} \hat{H}_i - \sum_j \dot{m}_{j,out} \hat{H}_j + \dot{Q} - \dot{W}_s = \sum_i F_{i,in} H_i - \sum_j F_{j,out} H_j + \dot{Q} - \dot{W}_s$$

Focus on the molar format, as we will modify this to extract the delta H's that we know.

$$\frac{d(N_A c_{p,A} T)}{dt} = \sum_i F_{i,in} H_i - \sum_j F_{j,out} H_j + \dot{Q} - \dot{W}_s$$

Apply steady state condition. Neglect shaft work.

$$0 = F_{A,in} H_{A,in} + F_{C,in} H_{C,in} - F_{C,out} H_{C,out} - F_{B,out} H_{B,out} + \dot{Q}$$

Add and subtract the terms $\pm F_{A,in} H_{A,out} \pm F_{C,in} H_{C,out}$. We need to do this to get enthalpy differences that we know into the enthalpy balance, as absolute enthalpies have little meaning.

$$0 = F_{A,in} (H_{A,in} - H_{A,out}) + F_{C,in} (H_{C,in} - H_{C,out}) + \dots$$

$$+ F_{A,in} H_{A,out} - (F_{C,out} - F_{C,in}) H_{C,out} - F_{B,out} H_{B,out} + \dot{Q}$$

Use the extent of reaction definition from the mass balances to simplify the expression and extract the heat of reaction:

$$\xi = \frac{(F_{C,out} - F_{C,in})}{2} = F_{A,in} = F_{B,out}$$

$$0 = F_{A,in} (H_{A,in} - H_{A,out}) + F_{C,in} (H_{C,in} - H_{C,out}) + \xi [H_{A,out} - H_{B,out} - 2H_{C,out}] + \dot{Q}$$

Recall the definition of the enthalpy of reaction

$$\Delta H_{rxn}(T_R) = \sum_{\text{products}} |v_i| H_i(T_R) - \sum_{\text{reactants}} |v_i| H_i(T_R) = H_B(T_R) + 2H_C(T_R) - H_A(T_R)$$

Since the reaction enthalpy is approximately independent of T near T_R and the reaction occurs at the reactor outlet temperature (also the reactor temperature), the energy balance becomes:

$$0 = F_{A,in} (H_{A,in} - H_{A,out}) + F_{C,in} (H_{C,in} - H_{C,out}) - \xi \Delta H_{rxn} + \dot{Q}$$

Putting the energy balance back in terms of mass (more convenient for this problem) we have:

$$0 = \dot{m}_{A,in} (\hat{H}_{A,in} - \hat{H}_{A,out}) + \dot{m}_{C,in} (\hat{H}_{C,in} - \hat{H}_{C,out}) - (k(T_R) m_A \Delta \hat{H}_{rxn}(T_R)) + \dot{Q}$$

Now we need to know how to calculate the enthalpy differences in the inflow streams: we need to heat up the inflow to the reaction temperature, T_R .

$H_{A,in}$ = molar enthalpy of liquid ammonium nitrate at 200 °F.

$H_{A,out}$ = molar enthalpy of liquid ammonium nitrate at T_R

$H_{C,in}$ = molar enthalpy of liquid water at 200 °F

$H_{C,out}$ = molar enthalpy of steam at T_R

$$(\hat{H}_{C,in} - \hat{H}_{C,out}) = (\hat{H}(\text{water}, 200^\circ F) - \hat{H}(\text{steam}, 500^\circ F)) + (\hat{H}(\text{steam}, (500^\circ F)) - \hat{H}(\text{steam}, T_R))$$

$$(\hat{H}_{C,in} - \hat{H}_{C,out}) = (-2.2 \text{ MJ/kg}) - (T_R - 500^\circ F) \left(2 \frac{\text{kJ}}{\text{kgF}^\circ} \right) \left(\frac{1 \text{ MJ}}{1000 \text{ kJ}} \right) = \left(-1.2 - \frac{T_R}{500^\circ F} \right) \text{ MJ/kg}$$

$$(\hat{H}_{A,in} - \hat{H}_{A,out}) = -(T_R - 200^\circ F) \left(\frac{0.8 \text{ kJ}}{\text{kgF}^\circ} \right) = -(0.8 T_R - 160^\circ F) \text{ kJ/kg} = -\frac{(0.8 T_R - 160^\circ F)}{1000} \text{ MJ/kg}$$

Solving the energy balance for the heat required for isothermal operation at 510 Fahrenheit we find:

$$0 = \dot{m}_{A,in} (\hat{H}_{A,in} - \hat{H}_{A,out}) + \dot{m}_{C,in} (\hat{H}_{C,in} - \hat{H}_{C,out}) - (k(T_R) m_A \Delta H_{rxn}(T_R)) + \dot{Q}$$

$$\dot{Q} = -\dot{m}_{A,in} (\hat{H}_{A,in} - \hat{H}_{A,out}) - \dot{m}_{C,in} (\hat{H}_{C,in} - \hat{H}_{C,out}) + (k(T_R) m_A \Delta H_{rxn}(T_R))$$

$$\dot{Q} = -(0.83)(140\text{kg/h})\left(-\frac{(0.8(510^\circ F) - 160^\circ F)}{1000}\text{MJ/kg}\right) + \dots$$

$$-(0.17)(140\text{kg/h})\left(-1.2 - \frac{(510^\circ F)}{500F^\circ}\right)\text{MJ/kg} + \dots$$

$$(0.307\text{h}^{-1})(378.5\text{kg})(-0.740\text{MJ/kg})$$

$$\dot{Q} = 28.8\text{MJ/h} + 52.8\text{MJ/h} - 86.0\text{MJ/h} = -4.4\text{MJ/h}$$

If $T_a = 100^\circ\text{F}$, then we may find UA (given that there is excess cooling water, assume that the temperature change in the cooling water is negligible).

$$\dot{Q} = UA(T_a - T_R)$$

$$\dot{Q}/(T_a - T_R) = UA = \frac{-4.4\text{MJ/h}}{(100 - 510)F^\circ} = 0.01073\text{MJ/hF}^\circ = 0.00298\text{kW/}^\circ\text{F}$$

During the investigation, it was hypothesized that the temperature increased, accelerating the reaction. The rate constant of the decomposition reaction increases with temperature, e.g. at $T=560^\circ\text{F}$, $k=2.91\text{ hr}^{-1}$. The reaction follows the Arrhenius T-dependence.

Given two T values and two k values, calculate k(T). Note that in an Arrhenius expression, an ABSOLUTE temperature scale must be used. Recall the temperature in Rankine (an absolute scale) is just the Fahrenheit temperature plus 459.67.

$$k(T/^\circ\text{F}) = A \exp\left(\frac{-b}{T/^\circ\text{F} + 459.67}\right)$$

$$k(510) = A \exp\left(\frac{-b}{510 + 459.67}\right)$$

$$k(560) = A \exp\left(\frac{-b}{560 + 459.67}\right)$$

$$-\ln\left(\frac{k(510)}{k(560)}\right) = -\ln\left(\frac{0.307}{2.91}\right) = \left(\frac{b}{510 + 459.67}\right) - \left(\frac{b}{560 + 459.67}\right)$$

$$2.24906 = (5.0692E - 05)b$$

$$b = 44367$$

$$A = k(510) / \exp\left(\frac{-44367}{510 + 459.67}\right) = 2.28E19\text{h}^{-1}$$

Note that k(T) is very sensitive to small changes in the activation energy (or b in this case).

$$b = \frac{E_a}{R} (\text{Rankine})$$

(c) Using the stability criteria explained in the vicinity of Eq. 8-75, should the reactor operate stably at 510°F? What is the critical temperature above which runaway reaction could occur?

This question is very poorly worded as to its intent. The intent is to ask you to do a stability analysis on the steady state at 510°F and see if a perturbation could lead to a hotter, higher conversion steady state.

Define $G(T)$ and $R(T)$ as follows:

$$G(T) = \frac{-km_A \Delta \hat{H}_{rxn}}{\dot{m}_{A,in}} = \text{energy produced per unit mass of A fed. One}$$

could also define $G(T)$ as energy produced per mole fed, as it is in Fogler, but mass is a more convenient basis in this problem.

$G(T) = R(T)$ at steady state: $R(T)$ is all the rest of the terms in the enthalpy balance (multiplied by -1, divided by the mass flow rate in)

$$R(T) = \frac{-\dot{m}_{A,in} (\hat{H}_{A,in} - \hat{H}_{A,out}) - \dot{m}_{C,in} (\hat{H}_{C,in} - \hat{H}_{C,out}) - \dot{Q}}{\dot{m}_{A,in}}$$

Near a steady state, there is no accumulation of A in the reactor and:

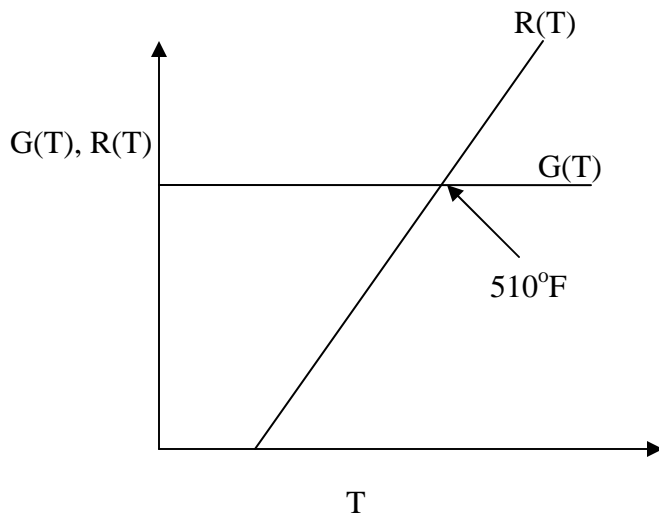
$$\dot{m}_{A,in} = km_A$$

Thus $G(T)$ simplifies to:

$$G(T) = -\Delta \hat{H}_{rxn}$$

Since there is no outflow, the conversion must always be unity. This makes the $G(T)$ curve much simpler than it is in the standard CSTR in Fogler.

Also notice that $R(T)$ is a simple linear function of T . Thus if we sketch $R(T)$ and $G(T)$, the following results:



Since both $G(T)$ and $R(T)$ are lines, there is only one possible intersection and one possible steady state. If you perturb the steady state to a slightly hotter temperature, $R > G$ and the system will cool down. If you perturb the system to a slightly cooler temperature, $G > R$ and the system will warm up. Thus the steady state is STABLE.

Stability analysis is only useful for small perturbations from a steady state. Determining the magnitude of a perturbation that will cause the system to "blow up" is beyond the scope of the problem.

The analysis in Fogler is to find perturbations that cause motion from one low-temperature steady state to a higher temperature steady state (ignition). As this transition is not possible given our G and R curves, the analysis required is much simpler.

It is believed that pressure fluctuations were detected in the feed stream and it was shut off by a plant operator about 4 minutes before the explosion occurred.

(d) Write and (using Matlab) solve a set of differential equations describing what happened in the reactor after the feed was shut off. Plot the temperature in the reactor vs. time. Do you predict an explosion?

Unsteady Problem

$$m_A(t=0) = 378.5 \text{ kg}$$

$$T(t=0) = 510^\circ F$$

Batch Reactor Balances: for subtle reasons, it is not possible to just set the inflow terms in the CSTR energy balance to zero.

Given that there is negligible gas holdup in the reactor:

$$N_B(t) = N_C(t) = 0$$

hence,

$$\frac{dN_B}{dt} = \frac{dN_C}{dt} = 0$$

Enthalpy:

$$\frac{dH}{dt} = \frac{d(N_A H_A + N_B H_B + N_C H_C)}{dt} = \frac{d(N_A H_A)}{dt} = \frac{dN_A}{dt} H_A + \frac{dH_A}{dt} N_A$$

$$\frac{dH}{dt} = \dot{Q} - F_{B,out} H_B - F_{C,out} H_C$$

$$\frac{dN_A}{dt} H_A + \frac{dH_A}{dt} N_A = \dot{Q} - F_{B,out} H_B - F_{C,out} H_C$$

Batch Reactor mole balances

$$\frac{dN_A}{dt} = -kN_A$$

$$\frac{dN_B}{dt} = 0 = -F_{B,out} + kN_A$$

$$F_{B,out} = kN_A$$

$$\frac{dN_C}{dt} = 0 = -F_{C,out} + 2kN_A$$

$$F_{C,out} = 2kN_A$$

Plugging in the three mole balance relationships into the enthalpy balance we find:

$$-kN_A H_A + \frac{dH_A}{dt} N_A = \dot{Q} - kN_A H_B - 2kN_A H_C$$

$$\frac{dH_A}{dt} N_A = \dot{Q} - kN_A (H_B + 2H_C - H_A) = \dot{Q} - kN_A \Delta H_{rxn}(T)$$

$$\frac{dH_A}{dt} = c_{p,a} \frac{dT}{dt}$$

$$\frac{dT}{dt} = \frac{\dot{Q} - kN_A \Delta H_{rxn}(T)}{N_A c_{p,a}} = \frac{\dot{Q} - km_A \Delta \hat{H}_{rxn}(T)}{m_A \hat{c}_{p,a}}$$

$$k(T/^{\circ}F) = A \exp(-b/(T + 459.67))$$

$$\Delta H_{rxn}(T) \approx \Delta \hat{H}_{rxn}(510^{\circ}F)$$

Now we have an ode set and initial conditions for a Matlab simulation:

$$m_A(t=0) = 378.5 \text{ kg}$$

$$T(t=0) = 510^{\circ}F$$

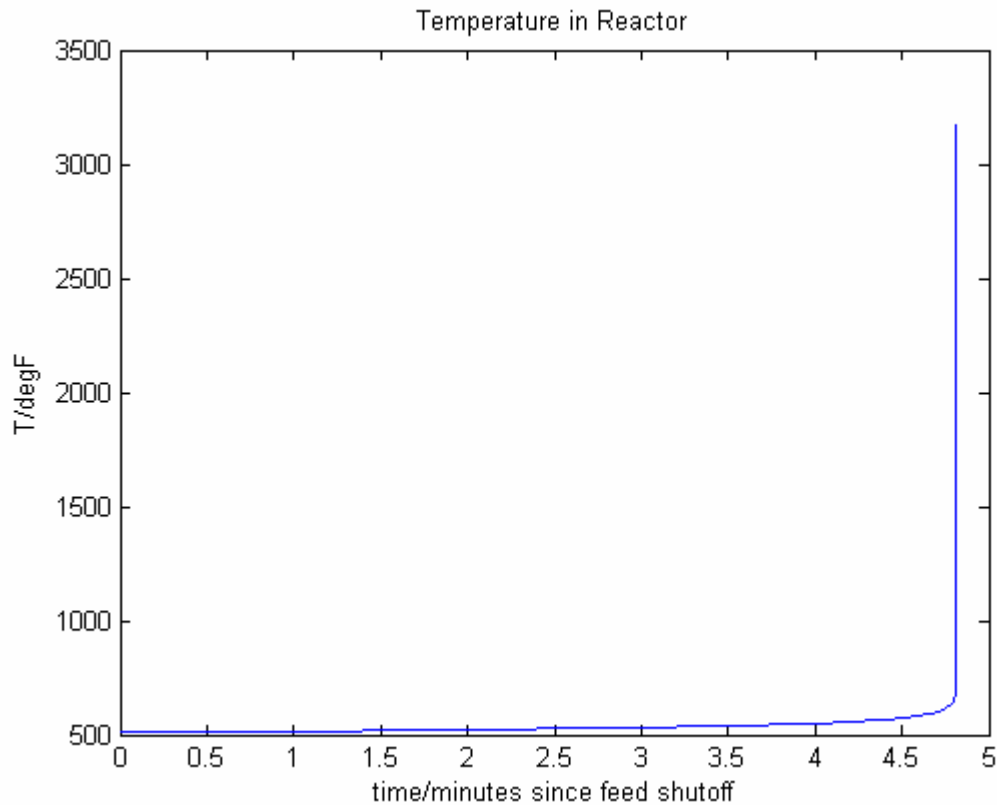
$$\frac{dm_A}{dt} = -k(T)m_A$$

$$\frac{dT}{dt} = \frac{UA(T_a - T)}{m_A \hat{c}_{p,a}} + \frac{-k(T)\Delta \hat{H}_{rxn}}{\hat{c}_{p,a}}$$

Code:

```
function [m,T]=hw6p1(tminutes);
%[m,T]=hw6p1(5); %run simulation for 5 minutes, crashes at ~4.5 minutes
thours = tminutes/60;
x0 = [378.5;510];
options = odeset('RelTol',10^-6,'AbsTol',10^-9);
[t,x] = ode15s(@odefun,[0,thours],x0,options);
m = x(:,1);
T = x(:,2);
figure(1);
plot(t*60,m);
title('NH_4NO_3 holdup');
xlabel('time/minutes since feed shutoff')
ylabel('m')
figure(2);
plot(t*60,T);
title('Temperature in Reactor');
xlabel('time/minutes since feed shutoff')
ylabel('T/degF')
return;
function derivs = odefun(t,x)
m = x(1); %kg NH4NO3
T = x(2); %degF
k = 2.28e19 *exp(-44367/(T+459.67));
UA = 0.01073; %MJ/(h degF)
Ta = 100; %degF
cpa = 0.8/1000; %MJ/(kg NH4NO3 degF)
dHrxn = -0.740; %MJ/kg NH4NO3
dmdt = -k*m;
%dTdt = (-k*dHrxn/cpa) + (UA*(Ta-T)/(m*cpa)) + (T*k); %slightly wrong
dTdt = (-k*dHrxn/cpa) + (UA*(Ta-T)/(m*cpa)); %correct
derivs = [dmdt;dTdt];
return;
```

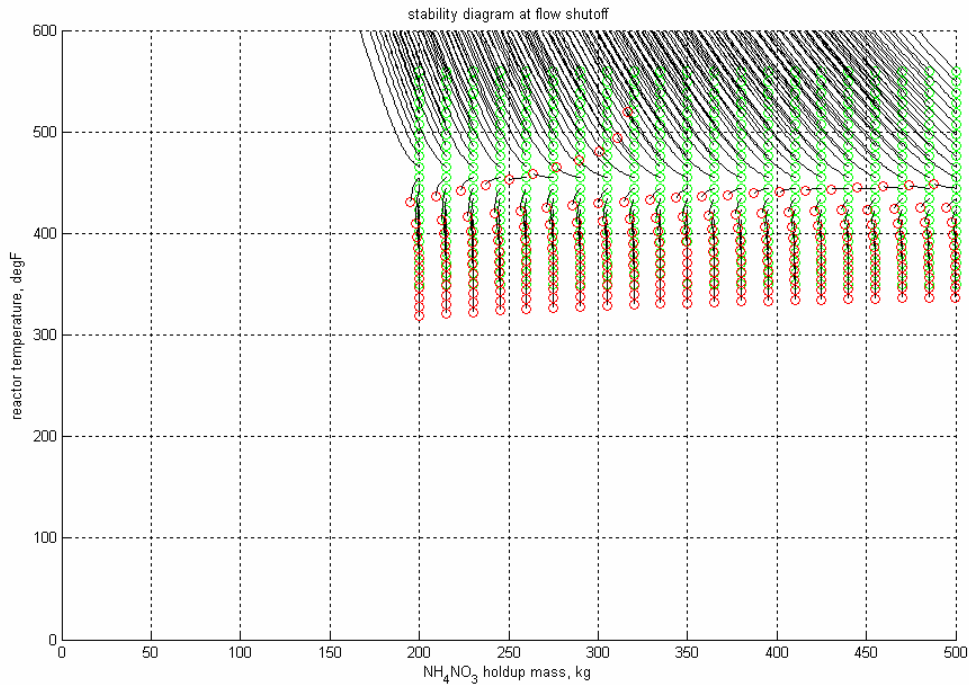
Temperature Plot:



Perturbing the most sensitive problem parameter, the activation energy term, b , by $\pm 1\%$ gives similar looking plots with explosion times shifted to 3-8 minutes.

(e) Was the operator wise to quickly shut off the feed of aqueous ammonium nitrate solution when he feared something was going wrong in the reactor? Is there something else he should have done to prevent the disaster?

The shutoff of the reactor turned a stable steady-state system of operation into an unsteady system, far from a steady state. Steady state in the batch reactor would mean the reactor is empty at 100°F . In order for the batch reactor to reach this steady state, the reactor must cool down. One can plot mass-temperature trajectories of the reactor operating in batch mode given different initial holdup masses and temperatures.



Green circles represent initial conditions, red circles represent final conditions after 4 hours of integration. Black lines represent trajectories and connect green circles to red ones. Diverging trajectories lead to a temperature "explosion". The absolutely final steady state would be an empty reactor at the temperature of the cooling water.

It is clear that above ~425°F it is not safe to shut off the reactor; this threshold "safety limit" temperature increases slightly as mass holdup decreases. Since the initial conditions are above this threshold, the sudden shutoff of the feed was a BAD IDEA.

In order to prevent the disaster, one must cool the reactor below the critical mass/temperature line before shutting off the feed. *This could be accomplished by injecting more water into the system, gradually decreasing the flow rate, increasing the cooling rate, etc.*

```

Code for part e:
function stabilitydiagram(tminutes);
%stabilitydiagram(240); %integrate trajectories for at most 240 minutes
thours = tminutes/60;
figure(3); clf; hold on;
options = odeset('RelTol',10^-6,'AbsTol',10^-9);
mlist = linspace(200,500,21);
Tlist = linspace(350,560,21);
for(i = 1:length(mlist))
    for(j=1:length(Tlist))
        [t,x] = ode15s(@odefun,[0,thours],[mlist(i),Tlist(j)],options);
        m = x(:,1);
        T = x(:,2);
        plot(m(end),T(end),'or'); %red stop
        plot(m(1),T(1),'og'); %green go
        plot(m,T,'-k'); %black trajectory
    end
end
title('stability diagram at flow shutoff')
xlabel('NH_4NO_3 holdup mass, kg')
ylabel('reactor temperature, degF')
xlim([0,500])
ylim([0,600])
grid on;
hold off;
return
function derivs = odefun(t,x)
m = x(1); %kg NH4NO3
T = x(2); %degF
k = 2.28e19 *exp(-44367/(T+459.67));
UA = 0.01073; %MJ/(h degF)
Ta = 100; %degF
cpa = 0.8/1000; %MJ/(kg NH4NO3 degF)
dHrxn = -0.740; %MJ/kg NH4NO3
dmdt = -k*m;
%dTdt = (-k*dHrxn/cpa) + (UA*(Ta-T)/(m*cpa)) + (T*k); %slightly wrong
dTdt = (-k*dHrxn/cpa) + (UA*(Ta-T)/(m*cpa)); %correct
derivs = [dmdt;dTdt];
return;

```

(f) Propose a procedure for safely starting-up and shutting-down a process like this (a qualitative description will suffice).

Examples of ideas:

The flowrate could be turned on/shut off gradually

The concentration of ammonium nitrate could be ramped up/down gradually

Greater cooling/heating control could be utilized at startup and shutdown