

Chemical Reaction Engineering - Part 10 - thermal safety

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Safety in chemical plants

Safety in chemical plants is an important topic for the workers, the people in the surrounding community, and the investors in the plant.

Safety should be considered in all aspects of plant design and operation:

- The process should be designed to minimize use of, storage of, and discharge of hazardous materials. Less hazardous and environmentally "green" chemistry and process steps should be sought.
- Equipment, control, and operational systems should be designed to be safe.
- Formal hazard and risk analysis studies should be performed during design, before maintenance, and before any changes are made to the process chemistry, equipment, or operational procedures.
- Equipment should be instrumented so that early warning of off-specification ("off-spec") conditions is given to operators.
- Operators should be trained on how to respond to warnings and off-spec conditions.
- Systems such as pressure relief systems should be in place in case process upsets occur.
- Accident response teams should be trained to respond in case accidents occur.

Special care must be taken before the following situations, because they are when most accidents occur:

- after changes are made to the chemistry, to equipment or to operational procedures
- during maintenance, especially during system shutdown and startup

If you are interested, you can have a career in chemical process safety. It is an interesting and important field.

Our interest here is in the safe operation of batch reactors.

Endothermic reactions tend to be safe in the absence of equipment failure. If heating of the reactor fails, the reactor will cool down and the reaction will slow down.

So our main interest here is in the safe operation of exothermic batch reactors. If cooling of the reactor fails, the reactor will heat up and the reaction will speed up.

That situation is called thermal "runaway."

Thermal runaway

In class we watched a video made by the U.S. Chemical Safety Board about thermal runaway in the T2 Laboratories plant, which made a gasoline octane enhancer, MMT or MCMT

<<https://www.youtube.com/watch?v=C561PCq5E1g>>. We also watched a short clip from the movie "Metropolis" when the giant machine started to go out of control and the operator watched the gauges

with alarm <<http://www.youtube.com/watch?v=0AY09DJkQMY>> (0:49 to 1:07).

What scared the operators in these two videos?

They became concerned when they saw an increase in the rate of increase of temperature. That is, when

$$\frac{d^2T}{dt^2} > 0 \quad \text{when} \quad \frac{dT}{dt} > 0$$

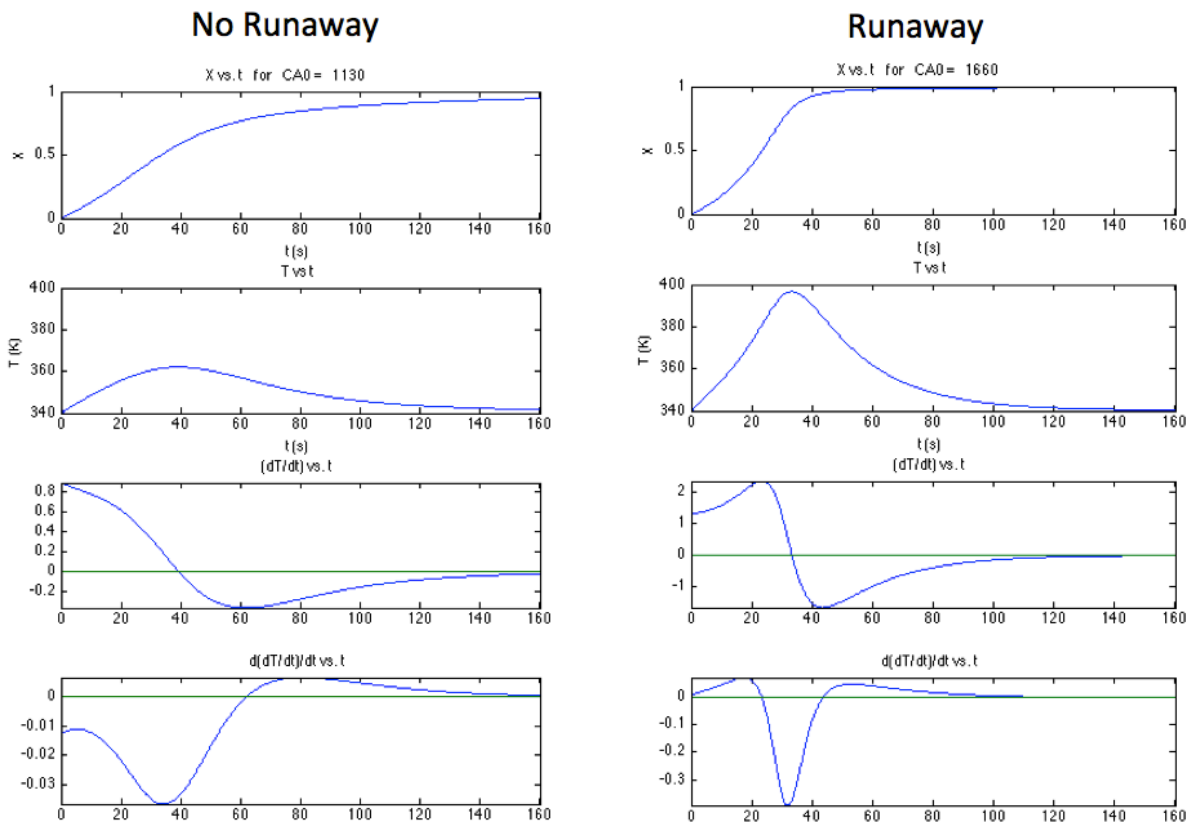
This is the mathematical definition of thermal runaway that is used in the research literature on the subject.

In some cases, your equipment may have been designed to handle even a rapid and adiabatic reaction. In that case, you don't have to worry as much.

However, this is the definition of thermal runaway that we will use during reactor design.

We wish to design a reactor that does not reach this condition of thermal runaway, at least when operating according to design.

Here are examples of a case with and without thermal runaway. The batch reactor has a cooling jacket. The panels, from top to bottom, plot versus time the following: X , T , dT/dt , and d^2T/dt^2 . All conditions are the same except for the initial reactant concentration. When the initial reactant concentration is increased, there is more reactant present in the reactor to convert and to release energy, and the initial reaction rate is faster.



Design criteria

There is a substantial research literature about design criteria for avoiding runaway. We will only touch on a few topics here.

Consider the simplified energy balance for a first-order, essentially irreversible reaction

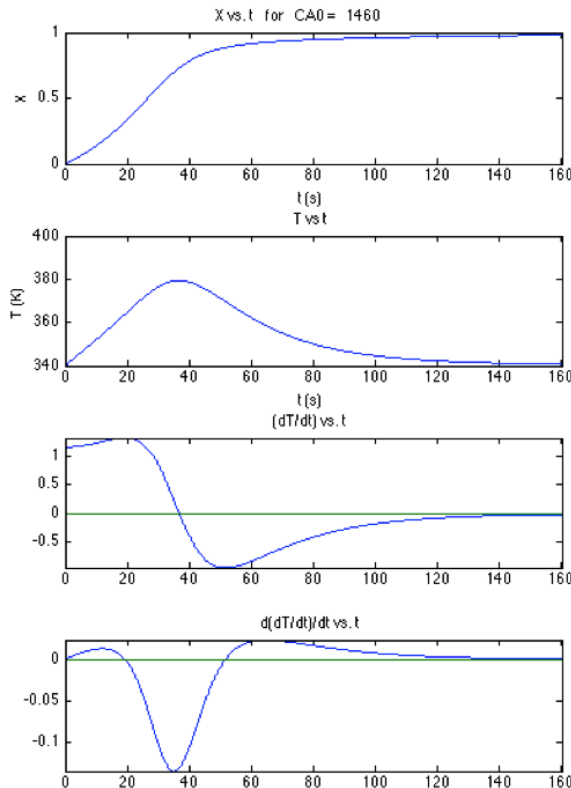
$$\frac{dT}{dt} = \left(\frac{UA}{\rho V C_{pm}} \right) (T_j - T) + \left(\frac{-\Delta H_{rxn}}{\rho C_{pm}} \right) k(T) C_{A0} (1 - X_A)$$

Consider the case where the jacket temperature equals the initial reactant temperature: $T_j = T(t = 0) = T_0$

$$\text{for } \frac{dT}{dt} = 0 \text{ at } t=0, X_A=0$$

$$C_{A0} = \frac{UA/V}{(-\Delta H_{rxn})k(T_0) \left(\frac{E}{RT_0^2} \right)}$$

where $k(T)$ is the value of the rate coefficient at T . Let's see what happens at this initial reactant concentration for this example system.



We see in the bottom panel that the second derivative is equal to zero initially but goes slightly positive at later time. So we need a more conservative criterion.

Professor H. Scott Fogler's web site discusses design criteria for runaway in Plug Flow Reactors (PFR), not batch reactors. But, as we will soon find out, batch reaction time is equivalent to PFR space time, which equals volume divided by volumetric flow rate
<http://www.umich.edu/~elements/08chap/html/runaway/index2.htm>.

One design criterion discussed is that from Froment and Bischoff.

$$\gamma = \frac{E}{RT_0} \quad \text{dimensionless activation energy}$$

$$\beta = \frac{(-\Delta H_{rxn})C_{A0}}{\rho C_{pm}T_0} \quad \text{dimensionless adiabatic temperature rise}$$

$$S = \beta \gamma \quad \text{dimensionless heat generation parameter}$$

$$N = \frac{(UA/V)}{C_{pm}(-r_{A0})M_w} \quad \text{dimensionless heat removal parameter}$$

where $(-r_{A0}) = k(T_0)C_{A0}$ for a first-order reaction, and $M_w =$ molecular weight of reactant A.

$$\frac{N}{S} = \frac{(UA/V)}{(-\Delta H_{rxn})(-r_{A0})} \left(\frac{RT_0^2}{E} \right) \frac{1}{x_{Am}} \quad \text{ratio of heat removal to generation}$$

where x_{Am} is the mass fraction of component A in the reactant mixture.

The design criterion for a first-order reaction is approximately

$$\frac{N}{S} \geq 0.5 + \log_{10}(S)$$

The safe ratio of heat removal to generation increases with an increase in the system's heat generation capability.

For zero-order reactions, N/S must be higher than for a first-order reaction (why? because the rate doesn't fall with concentration). For second-order reactions, N/S can be lower than for a first-order reaction (why? because the rate falls faster with concentration).

For a first-order, essentially irreversible reaction, when $x_{Am} = 1$, the case where $N/S = 1$ is equivalent to our earlier case of $d^2T/dt^2 = 0$ at $t = 0$. The above design criterion of Froment and Bischoff is more conservative. For the case in the plots above, $S = 5.70$ and $N/S = 1.19$, which means more cooling relative to generation (in our example, lower C_{A0}).

Fogler's web site discusses another, more conservative criterion.

To find the safe C_{A0} for specified conditions:

- Find C_A that is present at the T -maximum in one run (maximum in T vs. t)
- Find the maximum C_A that is present at the T -maximum of many runs
- This C_A is C_M and the corresponding T is T_M
- Find C_{A0} such that C_M is achieved at T_M
- Operate at that C_{A0}

For a first-order, essentially irreversible reaction,

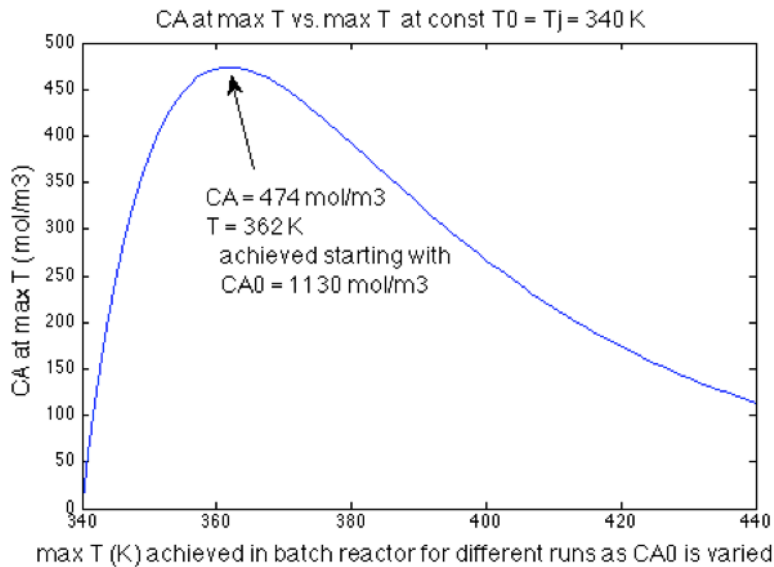
$$T_M = \frac{1}{2} \left[\frac{E}{R} - \sqrt{\frac{E}{R} \left(\frac{E}{R} - 4T_j \right)} \right]$$

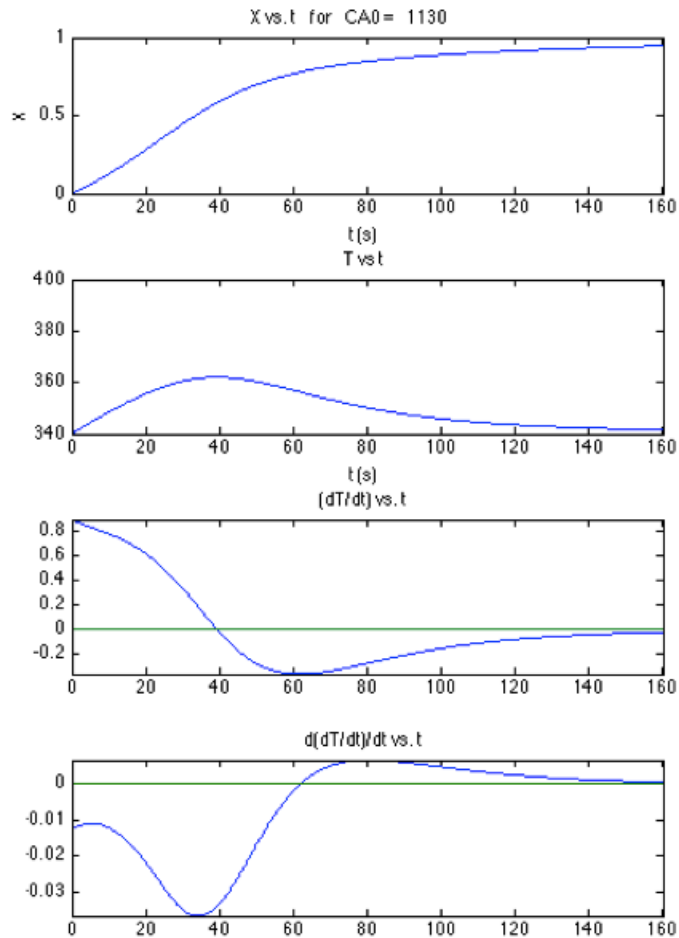
$$C_M = \max C_{A,m} = \frac{U A/V (T_M - T_j)}{(-\Delta H_{rxn}) k(T_M)}$$

where $k(T_M)$ is the value of the rate coefficient at T_M .

Higher safe C_{A0} = more money one batch can make.

Below are plots for the same case used for the plots above.





Additional resources

K. R. Westerterp and E. J. Molga, "Safety and Runaway Prevention in Batch and Semibatch Reactors - A Review," *Chemical Engineering Research and Design*, vol. 84, no. 7, pp. 543–552, Jul. 2006.

P. F. Nolan and J. A. Barton, "Some lessons from thermal-runaway incidents," *Journal of Hazardous Materials*, vol. 14, no. 2, pp. 233–239, 1987.

J. M. Zaldívar, J. Cano, M. A. Alós, J. Sempere, R. Nomen, D. Lister, G. Maschio, T. Obertopp, E. D. Gilles, J. Bosch, and F. Strozzi, "A general criterion to define runaway limits in chemical reactors," *Journal of Loss Prevention in the Process Industries*, vol. 16, no. 3, pp. 187–200, May 2003.

A. Milewska and E. Molga, "Safety aspects in modelling and operating of batch and semibatch stirred tank chemical reactors," *Chemical Engineering Research and Design*, vol. 88, no. 3, pp. 304–319, Mar. 2010.

Fogler's web site for runaway in Plug Flow Reactors (PFR) but, as we will soon find out, batch reaction time is equivalent to PFR space time = volume divided by volumetric flow rate

<<http://www.umich.edu/~elements/08chap/html/runaway/index2.htm>>

Matlab script for example plots

```

% 1st order reaction in batch reactor with heat exchange
clear all
kf300 = 1e-3; % 1/s, rate coefficient at 300 K
kb300 = 0; % 0.5e-3; % 1/s, rate coefficient at 300 K
Ef = 50; % kJ/mol, activation energy
% xxx Eb = 250;
DH = -150; % xxx Ef - Eb % kJ/mol, heat of reaction
Eb = Ef - DH;
R = 8.3145e-3; % kJ/mol/K, gas constant
Cpm = 2; % kJ/kg/K
rho = 1000; % kg/m3
cao = 1360; % 1130; % mol/m3, initial reactant conc
V = 0.1; % m3, volume of reactor contents
UA = 10; % 10; % kJ/K/s
To = 340; % 340, K, initial reactor T
Tj = To; % K, jacket T
i = 1; % index
x = 0;
t = 0;
T = To;
dt = 0.0001/kf300;
% while x(i) <= 0.95
% while t(i) <= 200
while x(i) <= 0.95
    kf = kf300*exp(-(Ef/R)*(1/T(i) - 1/300));
    kb = kb300*exp(-(Eb/R)*(1/T(i) - 1/300));
    rate = cao*(kf*(1-x(i)) - kb*x(i)); % mol/m3/s, (-rA)
    dxdt = rate/cao;
    dTdt = UA/(rho*Cpm*V)*(Tj - T(i)) - DH/(rho*Cpm)*rate;
    x(i+1) = x(i) + dxdt * dt;
    T(i+1) = T(i) + dTdt * dt;
    t(i+1) = t(i) + dt;
    i = i+1;
end
tt = sprintf('X vs. t for CA0 = %6.0f ',cao);
subplot(4,1,1), plot(t,x), title(tt)
ylabel('X'), xlabel('t (s)'), axis([0 max(t) 0 1])
subplot(4,1,2), plot(t,T), title('T vs t')
ylabel('T (K)'), xlabel('t (s)'), axis([0 max(t) To To+60])
dTdt = diff(T)/dt;
d2Tdt2 = diff(dTdt)/dt;
subplot(4,1,3), plot(t(1:length(t)-1),dTdt,[0 max(t)],[0 0]), title('(dT/dt) vs. t')
axis([0 max(t) min(dTdt)-0.00 max(dTdt)+0.00])
subplot(4,1,4), plot(t(1:length(t)-2),d2Tdt2,[0 max(t)],[0 0]), title('d(dT/dt)/dt vs. t')
axis([0 max(t) min(d2Tdt2)-0.000 max(d2Tdt2)+0.000])
maxT = max(T)
imt = find(T == max(T));
xAtMaxT = x(imt);
cAtMaxT = cao*(1-xAtMaxT)

% plot CA at max T vs. max T for these conditions
% conservative criterion to stay away from runaway conditions
% is to operate at CA0 at value that results in CA at max T
% during reaction

Tm = To:To+100;
kfm = kf300*exp(-(Ef/R)*(1./Tm - 1/300));
cam = UA/V*(Tm-Tj)./(-DH)./kfm;
xam = 1 - cam/cao;
figure(2)
plot(Tm,cam)
tt = sprintf('CA at max T vs. max T at const To = Tj = %3.0f K',To);
title(tt)
imc = find(cam == max(cam));
cAtMaxCam = cam(imc);
TatMaxCam = Tm(imc);
TM = 0.5*(Ef/R - sqrt(Ef/R*(Ef/R-4*Tj)))
kM = kf300*exp(-(Ef/R)*(1/TM - 1/300));
CM = UA/V*(TM-Tj)/(-DH)/kM

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% compute CA0 for d2T/dt2 (CT2) = 0
ko = kf300*exp(-(Ef/R)*(1/To - 1/300));
CT2 = UA/V/(-DH)/ko/(Ef/R/To^2)
% formula for d3T/dt3 (CT3) = d2T/dt2 = 0 gives unrealistic CA0
% CT3 = rho*Cpm/(-DH)/ko*sqrt(UA/(rho*V*Cpm))*To^2/sqrt((Ef/R)*(Ef/R - 2*To))
% xfac = rho*V*Cpm/UA/(1-2*R*To/Ef) % CT3/CT2, want < 1 but is > 1
DTadiab = (-DH)*cao/rho/Cpm
beta = DTadiab/To
gamma = Ef/R/To
S = beta*gamma
NoverS = 0.46+0.97*log10(S)

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