

## Chemical Reaction Engineering - Part 9 - thermal effects

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

### Energy balance for batch reactors

This energy balance was developed starting from an enthalpy balance and making the following simplifying specifications: no material flows into or out of system during reaction, negligible change in kinetic energy and potential energy, no phase change, constant volume, and heat capacity and heat of reaction are constant with composition and temperature.

$$\rho C_{pm} V \frac{dT}{dt} = Q + W + \Delta H_{rxn} r_A V$$

where  $\rho$  is density (kg/m<sup>3</sup>),  $C_{pm}$  is mass-average heat capacity (J/kg/K),  $Q$  (J/s) is the rate of heat transfer across heat transfer surfaces (coils or jackets) into the reactor,  $W$  (J/s) is the rate of non-PV work done on the reactor contents.

We are going to use this simplified energy balance so that we can see the main ideas more easily. Once you learn the main features, then you can go back and make corrections for changes in heat capacity and heat of reaction with changes in composition and temperature. The last section of these notes discusses these corrections. Also consult your thermodynamic textbook.

We may write this equation with negative signs in front of the heat of reaction and rate because the rate for reactant A is negative so negative rate is positive. And the negative of the heat of reaction for an exothermic reaction is positive.

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

Be careful to use the correct sign on heat of reaction (enthalpy change by reaction), since authors who always study exothermic reactions may quote positive numbers for the heat of reaction.

$W$  for batch reactors is usually energy input to the reactor contents by mixers, i.e., "shaft work." Except for very high rates of mixing or mixing of viscous fluids, this term is often negligible. The sign on  $W$  can change from author to author. For example some authors would write  $(-W)$  in the equation and define  $W$  as work done by the reactor contents.

The heat transfer term  $Q$  may be written as

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

$U$  (J/m<sup>2</sup>/K/s) is the overall heat transfer coefficient for the system.  $A$  (m<sup>2</sup>) is the heat transfer area.  $T_j$  (K) is the average temperature of the heat transfer fluid in the heat transfer jacket or coils.  $T$  is the temperature of the reactor contents, which are specified to be well mixed.

For negligible shaft work, we can write

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

$(-\Delta H_{rxn}) > 0$  for exothermic reactions, and  $(-r_A) > 0$  for reactant A.

Given input values, we are now able to solve some problems.

### Isothermal operation

What rate of energy supply or removal is required in order to maintain isothermal conditions?

$$Q = \Delta H_{rxn}(-r_A)V$$

For an endothermic reaction,  $\Delta H_{rxn} > 0$  and  $Q > 0$ , which means that energy must be supplied to the reactor contents. For an exothermic reaction,  $\Delta H_{rxn} < 0$  and  $Q < 0$ , which means that energy must be removed from the reactor contents.

The rate  $(-r_A)$  will vary with time, so  $Q$  varies with time. Since the temperature is constant, you can get the rate vs. time separately from the component balance equation. That is, at constant temperature, the energy balance and the component balance can be solved separately.

We can solve for how the heat transfer jacket temperature must vary with time.

$$0 = UA(T_j - T) + (-\Delta H_{rxn})(-r_A)V$$

$$T_j = T + \frac{\Delta H_{rxn}(-r_A)V}{UA}$$

For an endothermic reaction,  $\Delta H_{rxn} > 0$  so  $T_j > T$ . For an exothermic reaction,  $\Delta H_{rxn} < 0$  so  $T_j < T$ .

### Adiabatic operation

In this case,  $Q = 0$ . This condition can be approached in one or more of three ways: small  $U$ , small  $A$ ,  $T_j(t) = T(t)$ .

$$\rho C_{pm} V \frac{dT}{dt} = (-\Delta H_{rxn})(-r_A)V$$

$$\frac{dT}{dt} = \frac{(-\Delta H_{rxn})}{\rho C_{pm}}(-r_A)$$

Since  $T$  is changing with time, the rate coefficients in the rate equation will also change with time.

The component balance is

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

We could integrate both equations simultaneously after expressing  $(-r_A)$  in terms of conversion. It turns out that we can take advantage of the fact that the only factor affecting temperature is the reaction, in the absence of heat transfer.

$$(-r_A) = \frac{\rho C_{pm}}{(-\Delta H_{rxn})} \frac{dT}{dt} = \frac{N_{A0}}{V} \frac{dX_A}{dt}$$

$$dT = \frac{C_{A0}(-\Delta H_{rxn})}{\rho C_{pm}} dX_A$$

$$T - T_0 = \frac{C_{A0}(-\Delta H_{rxn})}{\rho C_{pm}} (X_A - 0)$$

$$T = T_0 + \frac{C_{A0}(-\Delta H_{rxn})}{\rho C_{pm}} X_A$$

This equation gives us the "adiabatic temperature rise" for exothermic reactions (or fall for endothermic).

Now that we have  $T$  as a function of  $X_A$ , we can put that solution for  $T(X_A)$  into the Arrhenius terms of the rate coefficients, and then integrate the balance equation separately by itself.

In an adiabatic reactor with an exothermic reaction, the temperature will rise, the rate coefficient value will increase, and the rate of reaction will speed up as reaction time progresses.

In an adiabatic reactor with an endothermic reaction, the temperature will fall, the rate coefficient value will decrease, and the rate of reaction will slow down as reaction time progresses.

In ReactorLab, Division 3, Lab 5 there is a simulation of a special type of adiabatic batch reactor - an adiabatic reaction calorimeter. That type of reactor is commonly used in process safety studies of new molecules or reactions. The reactor is used to measure the heat of reaction and activation energy for the new system. You want to make sure that your system can contain reactants and products in case of a runaway exothermic reaction. In fact, you want to design your system so a runaway situation is a very low probability.

### Non-isothermal, non-adiabatic operation

In this case, we have to integrate the component balance and the energy balance equations simultaneously. This is because the variables temperature  $T$  and conversion  $X_A$  appear in both differential equations and, because of the presence of heat transfer, we can't separate the two

differential equations as we did for adiabatic operation.

$$\frac{dX_A}{dt} = \frac{V}{N_{A0}}(-r_A)$$

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

where  $(-r_A)$  is a function of  $T$  and  $X_A$  in both equations.

We can integrate coupled differential equations numerically, e.g., using Euler's method. We can use the same logic as discussed earlier for Euler's method. We simply need to put both differential equations inside the loop that steps in time.

The heat transfer jacket or coil temperature  $T_j$  might be constant with time. Or  $T_j$  might change with time when a process controller is using  $T_j$  as the manipulated variable in order to control  $T$  at a set point value. That situation is discussed in your process control course (CENG 120 at UCSD). There is also a simulation of a related case at ReactorLab.net, Web Labs, Labs 3 and 4, and SimzLab's Control Lab, Division 2, Lab 1. Those simulations are for a continuous flow stirred tank reactor, not a batch reactor.

#### Example - isothermal operation

Here is a problem from an old exam. An example of the type of reactor used is a Mettler-Toledo RC1e.

A batch reactor with a fast-response heat transfer jacket was used as a reaction calorimeter. An automatic control system controlled the jacket temperature  $T_j$  in order to keep the temperature of the contents of the reactor constant at 360 K. The reaction is first-order in reactant A. (a) Determine the initial reaction rate in (mol/m<sup>3</sup>/min). (b) Determine the heat of reaction.

$t$ (min)	$C_A$ (mol/m <sup>3</sup> )	$T_j$ (K)
0	500	368.0
1.25	452	367.2
2.50	408	366.5
3.75	369	365.9
6.25	302	364.8
8.88	244	363.9

Show the proper sign on  $\Delta H$  and show units.  $V_{batch} = 2.0E-3$  m<sup>3</sup>,  $\rho = 1000$  kg/m<sup>3</sup>,  $C_p = 2.0$  kJ/kg/K,  $UA = 1.0$  kJ/K/min ( $\rho$  and  $C_p$  are for reactants). You may not need to use all of the data listed.

First, observe what is going on. Since  $T_j > T$ , there is net energy supply from the jacket to the reactor, so this is an endothermic reaction. We should get a value of  $\Delta H_{rxn} > 0$ . At longer time, the reaction slows down so the temperature difference ( $T_j - T$ ) gets smaller, since less energy has to be transferred into the reactor.

To work this quickly on an exam, use data at the first two times (0 and 1.25 min) to estimate the initial rate of reaction ( $-r_A$ ). Then use the energy balance to solve for the heat of reaction.

$$T_j = T + \frac{\Delta H_{rxn}(-r_A)V}{UA} \quad \text{from above, then rearrange to}$$

$$\Delta H_{rxn} = \frac{(T_j - T)UA}{(-r_A)V}$$

For these data,  $\Delta H_{rxn} = 100$  kJ/mol.

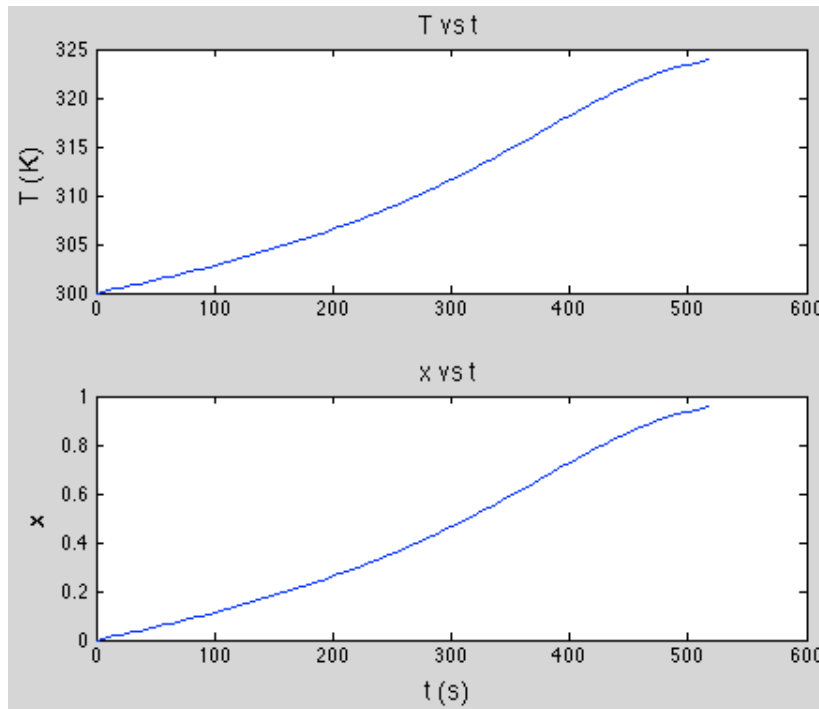
### Example - adiabatic operation

The Mettler-Toledo RC1e reactor can also be operated adiabatically by controlling the jacket temperature to equal the temperature of the reactor contents at all time. The TIAX Accelerating Rate Calorimeter is another type of lab reactor that can closely approach adiabatic operation.

In industry, adiabatic operation can be approached deliberately or can occur in accidents through loss of coolant. Process engineers doing risk analysis would simulate such an accident in order to design hazard containment systems, e.g., to capture and process discharge of the reactor contents.

Given the following data, estimate the time to reach 95% conversion and estimate the reactor temperature at that time. First-order, essentially irreversible reaction  $A \rightarrow B$ ,  $k(300 \text{ K}) = 0.001 \text{ s}^{-1}$ ,  $E = 100 \text{ kJ/mol}$ ,  $\Delta H_{rxn} = -100 \text{ kJ/mol}$ ,  $C_{pm} = 4 \text{ kJ/kg/K}$ ,  $\rho = 1000 \text{ kg/m}^3$ ,  $C_{A0} = 1000 \text{ mol/m}^3$ ,  $T(0 \text{ s}) = 300 \text{ K}$ .

The temperature at 95% conversion is 324 K at 518 s. Note that the rate first accelerates as the effect of increasing T on the rate coefficient is greater than the effect of decreasing reactant concentration. At high conversion, the rate is starting to slow down as the reactant concentration becomes small.



The Matlab script is listed below.

```
% adiabatic reactor example
clear all
k300 = 1e-3; % 1/s, rate coefficient at 300 K
E = 100; % kJ/mol, activation energy
R = 8.3145e-3; % kJ/mol/K, gas constant
delH = -100; % kJ/mol, heat of reaction
Cpm = 4; % kJ/kg/K
rho = 1000; % kg/m3
cao = 1000; % mol/m3, initial reactant conc
To = 300; % K, initial reactor T
% we can get T at 95% conversion by using the "adiabatic T rise" equation
% unit check: mol/m3 * kJ/mol * m3/kg * K kg/kJ = K
T95 = To + cao*(-delH)/rho/Cpm * 0.95
% for constant volume, 1st-order reaction
% dx/dt = k*(1-x)
% remember that k varies with T
% k(T) = k300*exp(-(E/R)*(1/T - 1/300))

% there may be an analytical integral but simple to do numerical soln
i = 1; % index
x = 0;
t = 0;
T = To;
% using constant dt, dt must be small relative to largest 1/k
% larger k, smaller dt needed for accurate integration
kmax = k300*exp(-(E/R)*(1/T95 - 1/300));
dt = 0.1/kmax;

while x(i) <= 0.95

    k = k300*exp(-(E/R)*(1/T(i) - 1/300));
    dxdt = k*(1-x(i));
    x(i+1) = x(i) + dxdt * dt;
    T(i+1) = To + cao*(-delH)/rho/Cpm * x(i+1);
    t(i+1) = t(i) + dt;
    i = i+1;

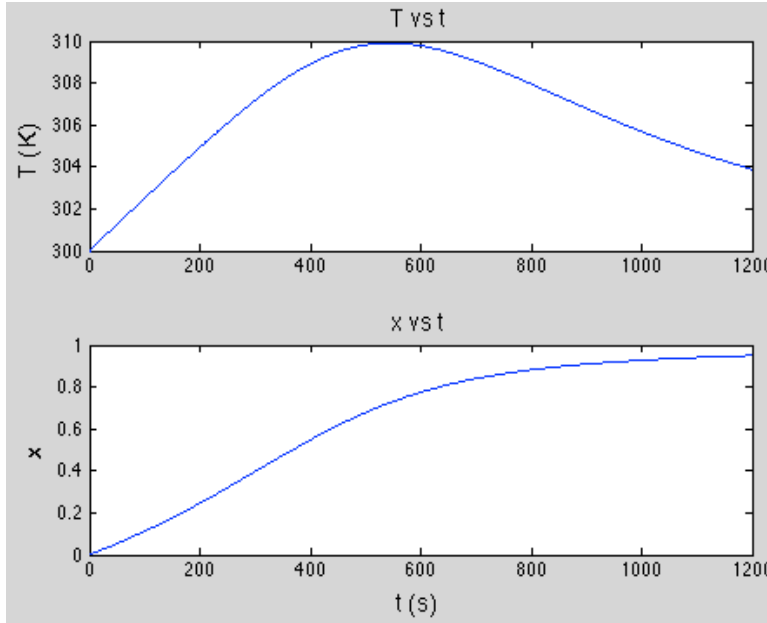
end

subplot(2,1,1), plot(t,T), title('T vs t')
ylabel('T (K)'), xlabel('t (s)')
subplot(2,1,2), plot(t,x), title('x vs t')
ylabel('x'), xlabel('t (s)')
```

### Example - non-isothermal, non-adiabatic operation

Consider the same system as above. However, instead of adiabatic operation, there is a heat transfer jacket with the following parameter values:  $UA = 1$  kJ/s/K,  $T_j = 300$  K, and reactor  $V = 0.1$  m<sup>3</sup>.

Conversion of 95% is reached at 1200 s and the final temperature is 304 K. The temperature goes through a maximum of 310 K. Can you explain this?



```
k300 = 1e-3; % 1/s, rate coefficient at 300 K
E = 100; % kJ/mol, activation energy
R = 8.3145e-3; % kJ/mol/K, gas constant
delH = -100; % kJ/mol, heat of reaction
Cpm = 4; % kJ/kg/K
rho = 1000; % kg/m3
cao = 1000; % mol/m3, initial reactant conc
To = 300; % K, initial reactor T
V = 0.1; % m3, volume of reactor contents
UA = 1; % kJ/K/s
Tj = 300; % K, jacket T
i = 1; % index
x = 0;
t = 0;
T = To;
dt = 0.001/k300;
while x(i) <= 0.95
    k = k300*exp(-(E/R)*(1/T(i) - 1/300));
    rate = k*cao*(1-x(i)); % mol/m3/s, (-rA)
    dxdt = rate/cao;
    dTdt = UA/(rho*Cpm*V)*(Tj - T(i)) - delH/(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
subplot(2,1,1), plot(t,T), title('T vs t')
ylabel('T (K)'), xlabel('t (s)')
subplot(2,1,2), plot(t,x), title('x vs t')
ylabel('x'), xlabel('t (s)')
```

## Effect of temperature on equilibrium conversion

All of the equations above with  $(-r_A)$  apply to both "reversible" and "essentially irreversible" reactions. When we have so-called "irreversible" reactions, we are talking about reversible reactions where the equilibrium conversion is almost 100% or, at least, much greater than the conversions in which we are interested.

For cases in which the equilibrium conversion is not almost 100%, we need to consider how equilibrium conversion changes with temperature. We also must include both the forward and back reaction terms in  $(-r_A)$ . Also refer back to CRE notes 04 on reversible reactions.

The equilibrium conversion will increase with increasing temperature for an endothermic reaction. The equilibrium conversion will decrease with increasing temperature for an exothermic reaction.

The Van 't Hoff equation shows how the equilibrium constant varies with heat of reaction and  $T$ .

$$\frac{d \ln K_{eq}}{dT} = \frac{\Delta H_{rxn}}{RT^2}$$

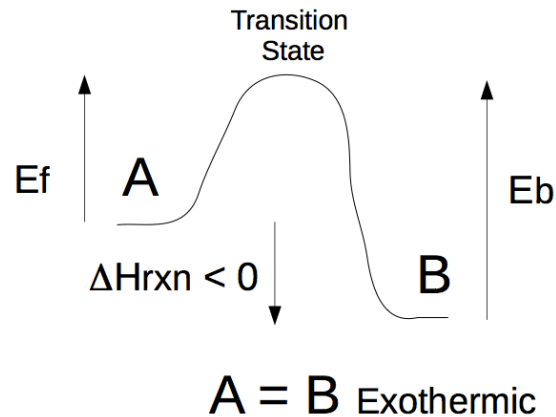
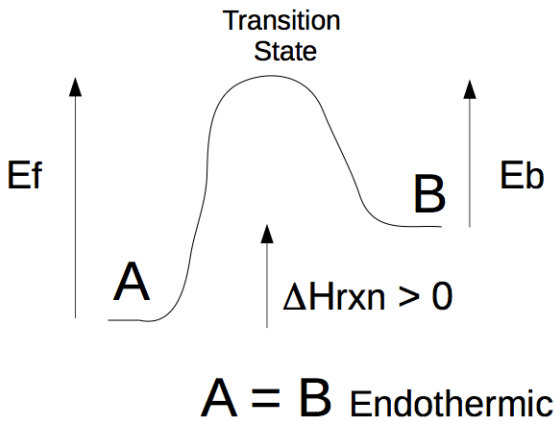
An easier way to see and remember how  $K_{eq}$  and  $X_{A,eq}$  vary with  $T$  is to consider the reaction  $A = B$ . The forward reaction is first-order in A and the back reaction is first-order in B for this example.

$$K_{eq} = \frac{k_f}{k_b} = \frac{A_f e^{-E_f/(RT)}}{A_b e^{-E_b/(RT)}} = \left(\frac{A_f}{A_b}\right) e^{-(E_f - E_b)/(RT)} = \left(\frac{A_f}{A_b}\right) e^{-\Delta H_{rxn}/(RT)}$$

$$\Delta H_{rxn} = E_f - E_b$$

For  $\Delta H_{rxn} > 0$  we have an endothermic reaction. Since  $E_f > E_b$ , as  $T$  increases, the rate of the forward reaction increases more than the rate of the back reaction increases. Both rates increase with temperature. Since the forward rate increases more, the equilibrium conversion increases with increasing  $T$ .  $K_{eq}$  increases with increasing  $T$ .

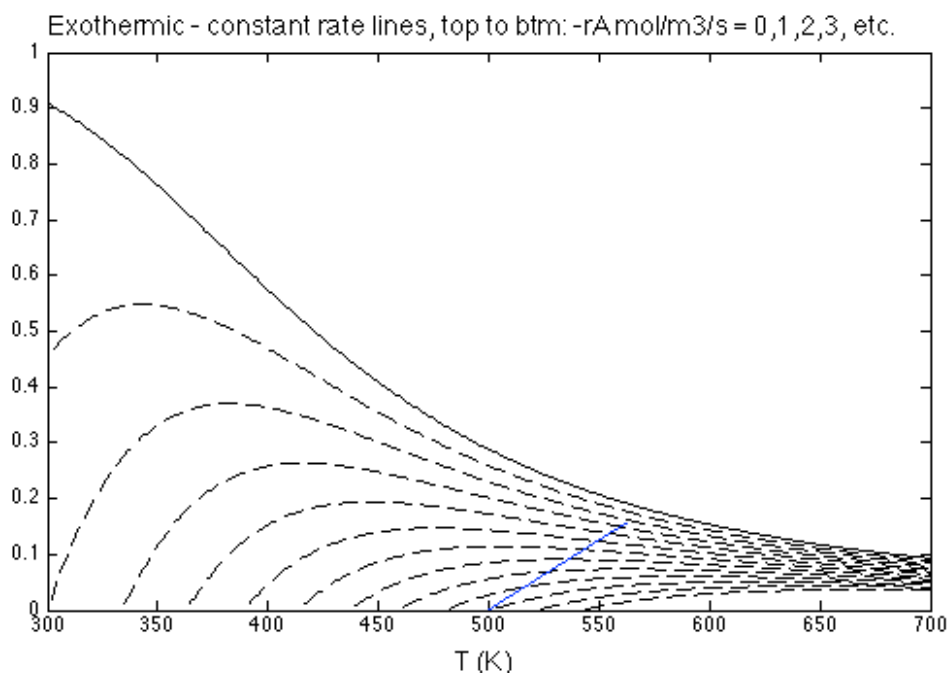
Here are sketches of energy vs. "reaction coordinate." The reaction proceeds from left to right.





For  $\Delta H_{rxn} < 0$  we have an exothermic reaction. Since  $E_f < E_b$ , as  $T$  increases, the rate of the forward reaction increases less than the rate of the back reaction increases. Both rates increase with temperature. Since the forward rate increases less, the equilibrium conversion decreases with increasing  $T$ .  $K_{eq}$  decreases with increasing  $T$ .

Here is a plot of conversion vs. temperature for an example exothermic reaction. Lines at constant net rate ( $-r_A$ ) are shown. The top line is for a net rate of zero. That solid line is the equilibrium line: a plot of  $X_{A,eq}$  vs.  $T$ . The Matlab script is listed below.



The blue line is the  $X$  vs.  $T$  path or "operating line" of an example adiabatic reaction. The equation for the line can be derived by rearranging the adiabatic temperature rise equation.

$$T = T_0 + \frac{C_{A0}(-\Delta H_{rxn})}{\rho C_{pm}} X_A$$

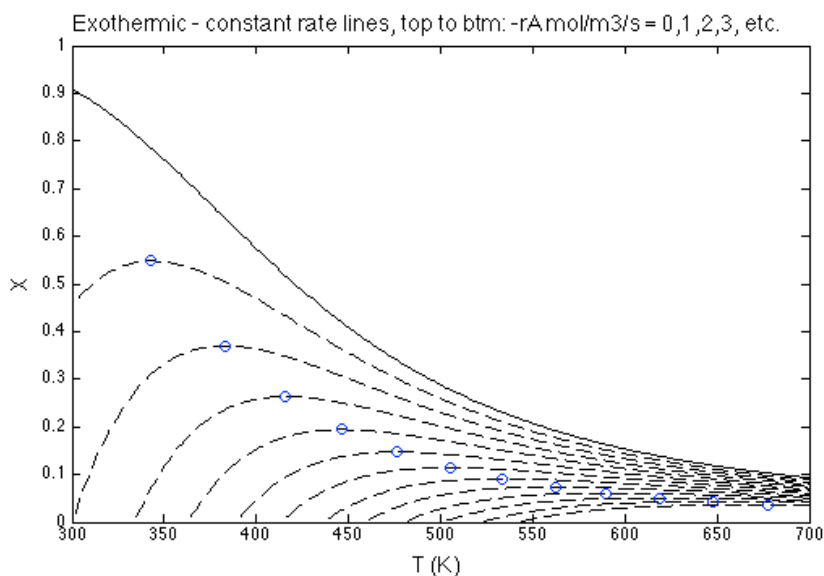
$$X_A = (T - T_0) \frac{\rho C_{pm}}{C_{A0}(-\Delta H_{rxn})}$$

For our simplified case of constant heat capacity and heat of reaction, adiabatic operating lines are straight. For a real case, they are slightly curved.

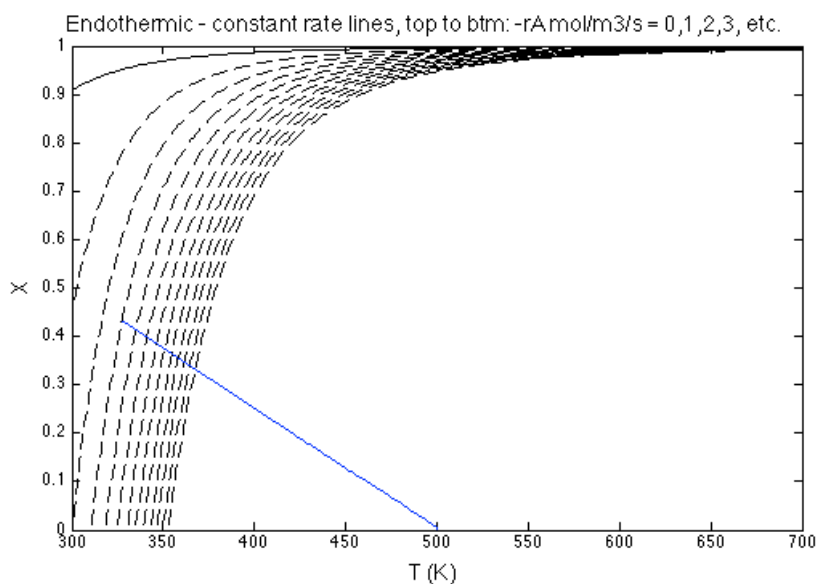
Given only the information on the plot, you can take the rates crossed by the blue line and plot them on a Levenspiel plot ( $1/-r_A$  vs.  $X_A$ ) to estimate the reaction time. For the blue line shown,  $t_{rxn} = 1000$  s.

An isothermal reaction would be represented by a vertical line on the plot. The operating line for a non-adiabatic, non-isothermal reaction would be curved.

This plot can be used to design the optimal progression of temperatures,  $T(t)$  optimal, that would result in achieving a given conversion in the shortest reaction time. Initially, at zero conversion, you would want to start at the maximum temperature at which your equipment can operate and at which no side reactions become important. Then, at higher conversions, you want to control the reactor temperature to the temperature at which the rate is highest at that temperature. That is, the operating line would follow the locus of the maxima of the constant rate lines on the  $X$  vs.  $T$  plot. For example, start at 678 K and run until the blue dot at 4% conversion, then follow the blue dots below, decreasing the temperature until you reach 55% conversion at 343 K. This temperature progression would get you to 55% in the shortest reaction time.



Below is the plot for an endothermic reaction and the operating line for an adiabatic reaction. This plot was generated by reversing the activation energy values for the forward and back reactions from the case above. Question: starting from your system's maximum temperature, what temperature or  $X$  vs.  $T$  progression would you use to reach a given conversion in minimum reaction time?



The Matlab script used to generate the three plots above is listed below.

```

clear all
kf300 = 5e-5; % 1/s, forward rate coefficient at 300 K
kb300 = 5e-6;
Ef = 10; % kJ/mol
Eb = 30; % kJ/mol
delH = Ef - Eb; % kJ/mol, heat of reaction, assume constant with T here
R = 8.3145e-3; % (kJ/mol/K), ideal gas constant
T = 300:700; % K, array of T values for plotting
kf = kf300*exp((-Ef/R)*(1./T - 1/300));
kb = kb300*exp((-Eb/R)*(1./T - 1/300));
K = kf./kb;
xeq = K./(1+K);
plot(T,xeq,'k')
axis([min(T) max(T) 0 1])
title('constant rate lines, top to btm: -rA mol/m3/s = 0,1,2,3, etc.')
ylabel('X')
xlabel('T (K)')
hold on

% add constant rate lines (-rA) > 0
rnet = [1 2 3 4 5 6 7 8 9 10 11 12];
[r c] = size(rnet);
% need to specify CA0 to associate numbers with constant rate lines > 0
cao = 40000; % mol/m3
for i = 1:c
    x = xeq .* (1 - (rnet(i)./(kf*cao)));
    % OPTIONAL for EXOTHERMIC: get (x,T) of max in this constant rate value vs. T
    [xm, im] = max(x);
    Tm = T(im);
    plot(T,x,'k--') % plot(T,x,'k--',Tm,xm,'bo')
end

% add example of X vs. T in adiabatic reaction
Cpm = 2; % kJ/kg/K, heat capacity, assume constant with T and composition
rho = 1000; % kg/m3
% initialize
% CLEAR ARRAYS ABOVE: set entire array to scalar initial value here
kf = 0;
kb = 0;
To = 500; % K, initial T, variable To used in while repeat below
T = To;
x = 0;
t = 0;
dt = 1; % s, time step
tfinal = 1000;
i = 1;
while t(i) < tfinal
    kf = kf300*exp((-Ef/R)*(1./T(i) - 1/300));
    kb = kb300*exp((-Eb/R)*(1./T(i) - 1/300));
    dxdt = kf*(1-x(i)) - kb*x(i);
    x(i+1) = x(i) + dxdt * dt;
    T(i+1) = To + x(i) * (-delH)*cao/rho/Cpm; % "adiabatic T rise eqn"
    t(i+1) = t(i) + dt;
    i = i+1;
end
plot(T,x)

```

## Effect of temperature on heat of reaction

Above we assumed the heat of reaction was constant with temperature in order to keep things simple while we learned the basics. Here are the equations for computing heat of reaction at different temperatures, starting with two equations showing differences in notation you might encounter between authors.

$$\Delta_r H(T_{ref}) = \Delta H_{rxn}^o \quad \text{heat of reaction (enthalpy change of reaction) at reference temperature}$$

$$\Delta_f H_i(T_{ref}) = \Delta H_{f,i}^o = H_i^o \quad \text{heat of formation of component } i \text{ at reference temperature}$$

$$\Delta H_{rxn}^o = \sum (\nu_i \Delta H_{f,i}^o)$$

$$\Delta H_{f,i}(T) = \Delta H_{f,i}^o + \int_{T_{ref}}^T C_{p,i} dT$$

You can often find the heat capacity of a component as a cubic equation in  $T$  in the literature.

For heat capacities that are approximately constant over the temperature range of interest,

$$\int_{T_{ref}}^T C_{p,i} dT \approx C_{p,i} (T - T_{ref})$$

Continuing with the heat of reaction,

$$\Delta H_{rxn}(T) = \sum \nu_i \left( \Delta H_{f,i}^o + \int_{T_{ref}}^T C_{p,i} dT \right)$$

$$\Delta H_{rxn}(T) = \Delta H_{rxn}^o + \sum \left( \nu_i \int_{T_{ref}}^T C_{p,i} dT \right)$$

$$\Delta H_{rxn}(T) \approx \Delta H_{rxn}^o + (T - T_{ref}) \sum (\nu_i C_{p,i})$$

$$\Delta H_{rxn}(T) \approx \Delta H_{rxn}^o + (T - T_{ref}) \Delta C_p$$

where

$$\Delta C_p \stackrel{\text{def}}{=} \sum (\nu_i C_{p,i}) \quad \text{for approximately constant } C_{p,i} \text{ over the } T \text{ range}$$

The heat capacities involved in calculating the heat of reaction are those of the reactant and product components only.

The average heat capacity  $C_{pm}$  in the reactor energy balance includes the heat capacities of all components in the reaction mixture, including those of any inerts or solvents.

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

### Additional resources

Schmidt's book - on library reserve & online via <http://roger.ucsd.edu/record=b7179459~S9>  
Chapter 5

Levenspiel's book - on library reserve  
Chapter 9

Fogler's *Essentials* book - on library reserve  
Chapter 13 - sections 13.1 to 13.3

Also see Fogler's web resources >> <http://www.umich.edu/~essen/html/13chap/frames.htm>