

Chemical Reaction Engineering - Part 2

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Strategy

What do we need to know how to do? You need to be able to write and solve material and energy balances along with thermodynamic equations. The understanding and practice you get in a CRE course will help everywhere you need to write and solve these equations, which is about everywhere in engineering.

Our strategy will be to focus on one type of reactor first: batch reactors. Reactants are loaded into a batch reactor, the reaction is started and runs for the time we specify, then the reactor is emptied and prepared for the next batch of reactants. There is no flow of chemicals in or out of the reactor during the reaction. You have probably used a batch reactor in the form of a test tube or flask in chemistry lab - or when you baked cookies or roasted a turkey. We will consider well-mixed batch reactors where conditions are uniform throughout the reactor at any given time.

After we get a good handle on batch reactors, we will go to other reactors. Next will be semi-batch reactors in which one or more reactants or products are selectively added to or removed from the reactor during the reaction. Then we will go to continuous reactors in which there is continuous flow of reactants into and products out of the reactor while reactions are occurring inside the reactor.

Component balance equation for batch reactors

General word equation for balance equations, component or energy, for any type of system.

$$\text{accumulation} = \text{in} - \text{out} + \text{generation by reaction}$$

First we will focus on component balances. The "accumulation" term for component A in a batch reactor is the rate of change of moles of that component in the control volume.

$$\frac{dN_A}{dt} \ll \text{the "accumulation" term}$$

The control volume is the entire contents of the batch reactor since we specify that they are well mixed. You can express the number of moles in terms of the volume of the control volume and concentration.

$$\frac{dN_A}{dt} = \frac{d(V C_A)}{dt} = V \frac{dC_A}{dt} \text{ for constant } V \ll \text{the "accumulation" term only}$$

The volume in the equation is the volume of the fluid contents. For liquids in a tank, the volume of the fluid contents will be less than the total internal volume of the tank in most cases.

The "in - out" terms are zero for a batch reactor during the period of interest, i.e., the time between loading and unloading during which the reaction occurs.

The "generation by reaction" term for component A is $r_A V$. For reactant components, which are components that decrease in quantity during reaction, the value of $r_A V$ is negative. For product components, the value of $r_A V$ is positive. For both reactants and products, this term is always written with a plus sign: $+r_A V$.

For a batch reactor for component A, the component balance is

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

The rate r_A is a function of N_A and quantities of other components, which we can relate to N_A using the stoichiometric equation of the reaction. So we have a differential equation to integrate from initial concentrations at time zero to final conditions at a final reaction time. The final conditions and time are often left as variables so that we can solve for different values of final conditions.

Rate equations

The rate of generation of A by reaction r_A will be a function of temperature T and the concentrations of other components present in the reactor including possibly catalysts and other components not appearing in the reaction's stoichiometric equation.

$$r_A = f(T, C_A, C_B, \text{etc.})$$

A common form of rate equation is the "power-law" rate equation. For reactant A,

$$r_A = -k C_A^\alpha C_B^\beta \dots$$

Note that the rate of generation of reactant component A has a negative value. Here, α is the "order" of the reaction in component A. Often we will discuss first-order and second-order rate equations.

$$r_A = -k C_A \quad \text{first order in A} ; \quad r_A = -k C_A^2 \quad \text{second order in A}$$

The rate coefficient k has a temperature dependence that will be approximated by the Arrhenius equation, which you have seen in chemistry courses.

$$k = A e^{-E/(R_g T)} \quad \text{where } A \text{ is the pre-exponential factor, and } E \text{ (or } \Delta E) \text{ is the activation energy}$$

This is another form that is useful in correlating data from experiments. It is the ratio of the Arrhenius equation at two temperatures.

$$k(T_2) = k(T_1) e^{-(E/R_g)(1/T_2 - 1/T_1)}$$

Reactions over solid catalysts may have Langmuir-Hinshelwood, Hougen-Watson (LHHW) rate equations. One example of an LHHW rate equation is

$$r_A = \frac{-k C_A}{1 + K_A C_A}$$

Note that at relatively large concentrations of reactant A for this rate equation, the rate can be zero-order in A.

$$r_A = -(k/K_A) = -k' = -k' C_A^0$$

LHHW rate equations have a denominator (inhibition term) that is related to the fact that a fixed area of solid catalyst surface can only hold a fixed maximum number of adsorbed molecules. Another example is

$$r_A = \frac{-k C_A}{(1 + K_A C_A)^2}$$

Note that at relatively large concentrations of reactant A for this rate equation, the rate can slow down (be "inhibited") with further increases in reactant concentration. This is called a negative-order rate equation.

$$r_A = -k' C_A^{-1}$$

Reactions catalyzed by enzymes are described by rate equations that are similar in form to LHHW equations. This is because a given quantity of enzyme molecules can only bind to a fixed maximum number of reactant molecules. In biological reactions, reactants are called "substrates." This form of rate equation for enzyme reactions is called a Michaelis-Menten rate equation.

$$r_A = \frac{-V_{max} C_A}{K_M + C_A} \quad \text{where } V_{max} \text{ is the maximum "velocity" or rate}$$

Do you see that this has the same functional form as the first LHHW rate equation listed above?

Dimensional units of rates and rate coefficients

We will use SI units as much as possible in these notes. The units of reaction rates are, for example,

$$r_A \left(\frac{\text{mol}}{\text{m}^3 \text{s}} \right) \quad \text{for "homogeneous" reactions, which occur in one-phase}$$

$$r_A \left(\frac{\text{mol}}{\text{kg s}} \right) \quad \text{for reactions catalyzed by solid "heterogeneous catalysts"}$$

Homogeneous reactions in this course will usually occur in either the gas or liquid phase.

For reactions catalyzed by heterogeneous catalysts, kg in the denominator of the units is the mass of catalyst, and mass of catalyst W ("weight") replaces V in the reactor balance.

$$\frac{dN_A(\text{mol})}{dt(\text{s})} = r_A \left(\frac{\text{mol}}{\text{kg s}} \right) W(\text{kg}) \quad \text{for reactions catalyzed by solid "heterogeneous catalysts"}$$

Alternatively, mass of catalyst could be replaced by volume of catalyst in the rate units. "Heterogeneous" because two or more phases are present.

Units of rate coefficients, k , vary with the equation. Rate coefficients are proportionality constants. They have whatever units are required to balance units.

In the denominator of LHHW rate equations, K_A has units of inverse concentration (or pressure) such that $K_A C_A$ (or $K_A P_A$) is dimensionless. In Michaelis-Menten rate equations, K_M has the same units as the concentration term. V_{max} has the same units as the rate r_A .

Conversion of limiting reactant

X_A is the "conversion" of the limiting or key (expensive) reactant A

$$X_A = \frac{N_{A0} - N_A}{N_{A0}}$$

First-order, essentially irreversible reaction

Consider the reaction $A = B$ where the forward and back (reverse) reactions are both first-order

$$r_A = -k_f C_A + k_b C_B$$

Now specify that we start with pure A and the conversion of component at equilibrium is almost complete. We say that a reaction is "essentially irreversible" or, loosely, "irreversible" when the reactant conversion at equilibrium closely approaches one. In that case, we can neglect the back reaction, except when we want to get very close to equilibrium conversion.

Specify that we have a constant volume, isothermal batch reactor. The component balance for A is

$$\frac{dC_A}{dt} = r_A = -k_f C_A \quad ; \quad \text{in terms of conversion} \quad \frac{dX_A}{dt} = k_f(1 - X_A)$$

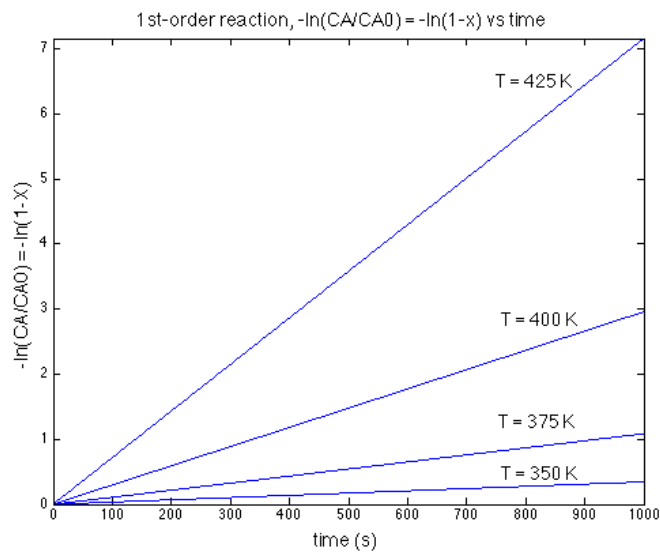
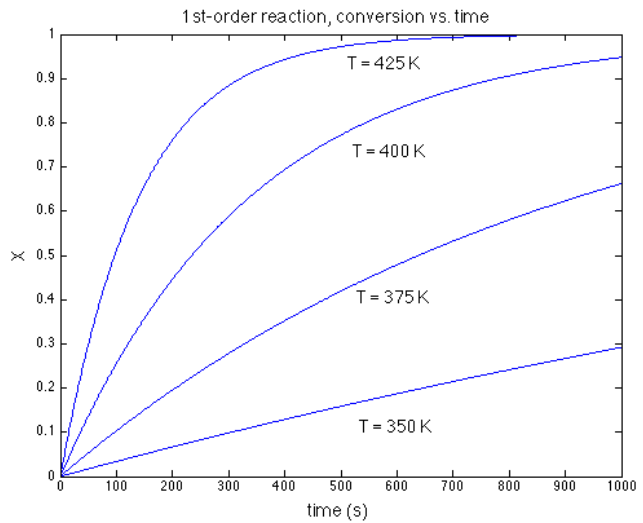
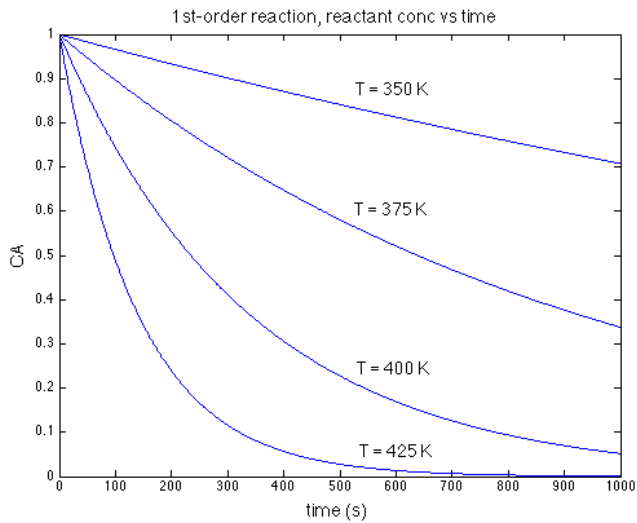
Separate variables, specify initial conditions, and integrate

$$\frac{dC_A}{C_A} = -k dt \quad ; \quad t=0 ; C_A(0) = C_{A,0} ; X_A(0) = 0 \quad ; \quad \frac{dX_A}{(1 - X_A)} = k dt$$

$$-\ln(C_A / C_{A,0}) = k t_{\text{rxn}} \quad ; \quad \text{in terms of conversion} \quad -\ln(1 - X_A) = k t_{\text{rxn}}$$

$$C_A = C_{A,0} e^{-kt_{\text{ran}}} \quad ; \text{ in terms of conversion } X_A = 1 - e^{-kt_{\text{ran}}}$$

Note that the conversion for a first-order reaction is not a function of the initial concentration of reactant. Why? When the concentration doubles, you need to react twice as many molecules to reach a given conversion but the rate also doubles, so you reach that conversion in the same amount of time.



Listing of Matlab script for the concentration vs. time plot above

```

% 1st-order essentially irreversible reaction
% plot conc vs time
A = 1e4; % (1/s), pre-exponential factor
E = 50e3; % J/mol, activation energy
R = 8.3145; % J/K/mol, ideal gas constant
Ca0 = 1; % mol/m3
t = 0:1:1000; % s, reaction time array
for T = 350:25:425
    k = A*exp(-E/R/T);
    Ca = Ca0*exp(-k*t);
    plot(t,Ca)
    hold on
    axis([0 max(t) 0 Ca0])
end
title('1st-order reaction, reactant conc vs. time')
ylabel('CA')
xlabel('time (s)')
hold off

```

Second-order, essentially irreversible reaction

$$r_A = -k C_A^2$$

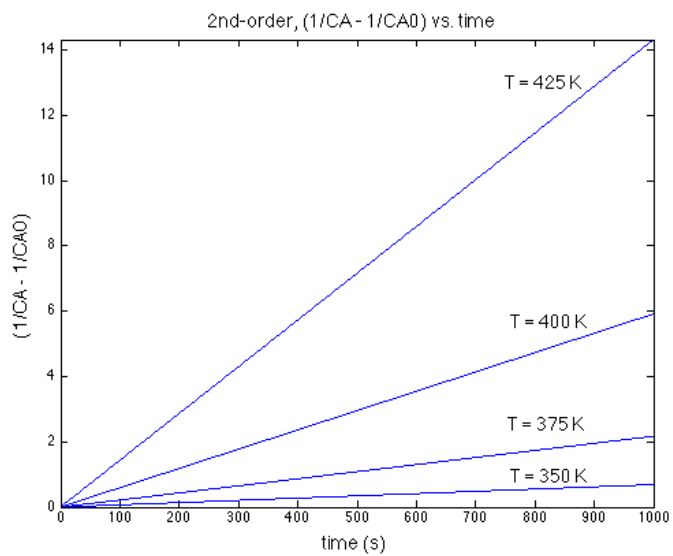
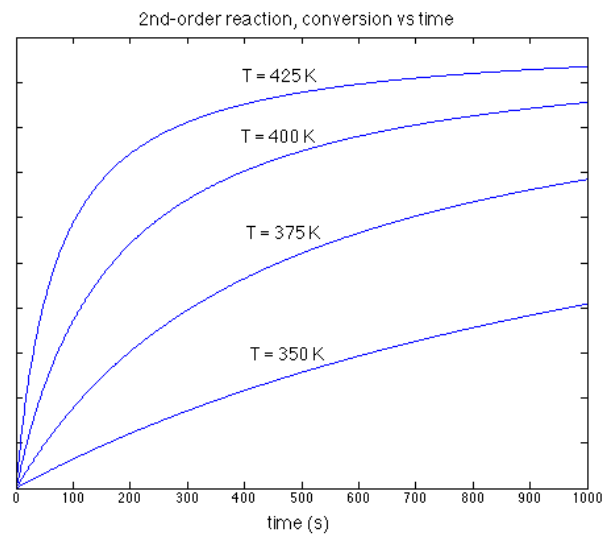
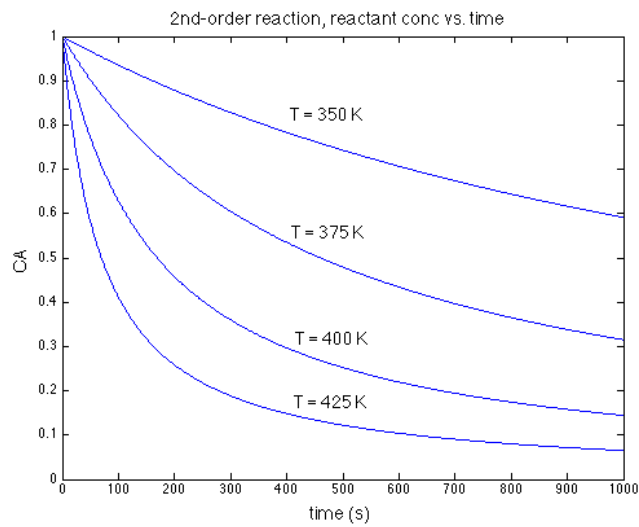
$$\frac{dC_A}{dt} = -k C_A^2$$

$$\frac{dC_A}{C_A^2} = -k dt$$

$$\left(\frac{1}{C_A} - \frac{1}{C_{A,0}} \right) = k t_{rxn}$$

$$C_A = C_{A,0} \left(\frac{1}{1 + C_{A,0} k t_{rxn}} \right) \quad ; \text{ in terms of conversion} \quad X_A = \frac{C_{A,0} k t_{rxn}}{1 + C_{A,0} k t_{rxn}}$$

Note that the conversion for a second-order reaction is a function of the initial reactant concentration, unlike the case for a first-order reaction. When the concentration doubles, you need to react twice as many molecules to reach a given conversion but the rate quadruples, so you reach that conversion in a shorter amount of time.



Matlab script for the linearized plot for 2nd order

```
% 2nd-order, essentially irreversible kinetics
A = 0.2e5; % m3/mol/s, pre-exponential factor
E = 50e3; % J/mol, activation energy
R = 8.3145; % J/K/mol
Ca0 = 1; % mol/m3, initial reactant conc
t = 0:1:1000; % s, reaction time array
for T = 350:25:425 % K, temperature
    k = A*exp(-E/R/T);
    Ca = Ca0*(1 ./ (1+Ca0*k*t)); % << NOTE ARRAY DOT OPERATOR ./
    Y = (1 ./ Ca - 1/Ca0)
    plot(t,Y)
    hold on
    axis([0 max(t) 0 max(Y)])
end
title('2nd-order, (1/CA - 1/CA0) vs. time')
ylabel('(1/CA - 1/CA0)')
xlabel('time (s)')
hold off
```

Batch cycle time

Time is needed (a) to fill a batch reactor, (b) to react, and (c) to empty the reactor and prepare it for the next batch. Batch reactors used to make food and pharmaceuticals need to be sterilized between batches and this takes time.

The entire time required for a batch is the "batch cycle time" t_{cycle} . The reaction time is t_{rxn} . We will call the sum of the other times the changeover time, t_{change} .

$$t_{cycle} = t_{rxn} + t_{change}$$

Both the reaction time and the changeover time affect the average production rate of a batch reactor. Given the desired average production rate and the cycle time, we can compute the amount of product that we need to produce in one batch:

$$\text{Amount of product per batch} = (\text{Desired average production rate}) (\text{batch cycle time})$$

Then we can determine the size of batch reactor needed to produce that amount of product in a batch.

For constant production rate and reaction time, as the changeover time increases, the size of the batch reactor must increase.

Starting and stopping batch reactions

In most of our examples, we will assume that the reaction can be turned on instantaneously at $t = 0$ and turned off instantaneously at t_{rxn} . This is not the case with real reactors. There will be some transition time to start the reaction and to stop it. As long as these transition times are much smaller than the reaction time, then our estimates will be good enough for most purposes.

How are reactions started and stopped? The exact ways will depend on the reaction and the equipment.

Starting may involve heating the reactor contents rapidly to the desired temperature. Below this temperature, the reaction rate may be very slow.

Starting may involve filling the reactor with all components except one of the reactants that is needed in small quantities, then adding that component.

Starting may involve filling the reactor with all components except the catalyst, then adding the catalyst.

Stopping may involve rapidly cooling or "quenching" the reactor contents. Stopping may involve adding a component like a radical scavenger to a chain reaction.

Stopping may involve letting the reaction run close to equilibrium conversion.

If starting or stopping takes significant time relative to the reaction time, then we need to write and solve the balance equations during those times.

Types of problems

We are starting with single reactions in isothermal batch reactors, so you need to be able to write and solve one ODE. Be able to write the component balance, check signs, and check units. Be able to identify the limiting reactant, write the stoichiometric equation such that the formal stoichiometric coefficient of the limiting (or key) reactant is -1, and define the conversion for that reactant. Be able to write a stoichiometric (mole) table when necessary, and know when you can save time by not writing one (see Part 2 stoichiometry). Know to use the stoichiometric table and ideal gas law for gases with changes in moles, pressure or volume. Be able to solve the component balance (see Part 3 integration).

There are several possible combinations of known values and unknown values. For example, all values given except reaction time, so find reaction time. Or all values given except final conversion, so find final conversion. Or given all values including final conversion, average production rate and batch changeover time, so find the batch volume.

We won't show examples of every possible combination of knowns and unknowns. You need to understand the basic principles so that you can solve for any combination you encounter.

Important new terms

batch reactor

well-mixed batch reactor

component balance

accumulation term

in - out terms

generation by reaction term

control volume

volume of the fluid contents vs. internal volume of tank, liquids vs. gases

power-law rate equation

first-order rate equation
second-order rate equation
zero-order rate equation
negative-order rate equation
Arrhenius equation
Langmuir-Hinshelwood, Hougen-Watson (LHHW) rate equation
Michaelis-Menten rate equation
limiting or key reactant
conversion of limiting or key reactant
homogeneous reaction
heterogeneous catalyst
equilibrium conversion
essentially irreversible or, loosely, "irreversible" reaction
batch cycle time
reaction time
changeover time
average production rate
quenching a reaction

Additional resources

First a comment. I am writing these notes as a result of feedback from students. In the past I required students to purchase a textbook. In all of the current texts, the three types of "ideal" reactors - batch, CSTR and PFR - are introduced at the start of the book and examples using all three are presented whenever a new topic is introduced (variable density, temperature effect, etc.). Some students found it confusing to handle both the switch of topic and switch of reactor type at the same time.

So my strategy with these notes is to focus on batch reactors only as we introduce most of the topics common to all reactors. Then proceed to the other types of reactors. So my reading suggestions will pick and choose sections as well as chapters.

If you find an explanation in a book that you think is good, please let me know. If you find the books confusing, then don't use them.

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

Chapter 1

Chapter 2 - sections 1, 3-5, 7, 9, 10.1-10.5, 16, 17

Levenspiel's book - on library reserve

Chapter 1

Chapter 2

Fogler's "Essentials" book - on library reserve for this course

Chapter 3

Fogler also has an older "Elements" book on reserve. Use the "Essentials" book if it is available. Chapter 3 and 4 of "Essentials" is Chapter 3 of "Elements."