

Chemical Reaction Engineering - Part 6

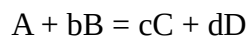
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Gas-phase reactions with change in total moles or volume or pressure

So far, we have been considering constant volume batch reactors. Here, we are going to discuss cases with gases where the reactor volume can change. We will also discuss gases in a constant volume reactor where the pressure changes because the total number of moles change with reaction.

First, you may wish to review Part 2 of these notes, which are on stoichiometry. We will repeat some of the equations here but not all of them

Consider this form of a stoichiometric equation.



where b, c and d are numbers and A, B, C and D are the names or formulae of the components.

The equation is written so that the coefficient of the limiting or key (important) reactant is one. If you are given an equation where this is not the case, just divide by a constant to get this form.

Now move all the reactants to the right hand side.

$$0 = -A - bB + cC + dD$$

This is the general form of a stoichiometric equation:

$$0 = \sum v_i a_i$$

where a_i are the names or formulae of the components, and v_i are the "formal stoichiometric coefficients." Here,

$$\begin{aligned} v_1 = v_A = -1 & \quad a_1 = A \\ v_2 = v_B = -b & \quad a_2 = B \\ v_3 = v_C = c & \quad a_3 = C \\ v_4 = v_D = d & \quad a_4 = D \end{aligned}$$

Note that the formal stoichiometric coefficients of the reactants are negative and those of the products are positive.

Write a stoichiometric table by writing the following equation for each component in the stoichiometric equation.

$$N_i = N_{i0} + v_i N_{A0} X_A$$

where X_A is the conversion of the limiting or key reactant A

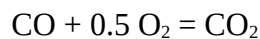
$$X_A = \frac{N_{A0} - N_A}{N_{A0}}$$

Conversions are dimensionless. If you are dealing with gases, also write a line for any inerts

$$N_{Inert} = N_{Inert0}$$

and then sum all the columns in the table to get the total number of moles of gas N_{tot} to use in computation of gas volume or pressure. In this course, we will use the ideal gas law unless told otherwise.

Here is an example for the gases CO, O₂, CO₂ and N₂ where CO is the limiting reactant.



Stoichiometric table (mole table)

$$\begin{array}{l} N_{CO} = N_{CO,0} - N_{CO,0} X_{CO} \\ N_{O_2} = N_{O_2,0} - 0.5 N_{CO,0} X_{CO} \\ N_{CO_2} = N_{CO_2,0} + N_{CO,0} X_{CO} \\ N_{N_2} = N_{N_2,0} \\ \hline N_{tot} = N_{tot,0} - 0.5 N_{CO,0} X_{CO} \end{array}$$

Note that, in general for a single reaction,

$$N_{tot} = N_{tot,0} \left(1 + \left(\sum v_i \right) y_{A,0} X_A \right)$$

Some authors, including Levenspiel and Fogler, define a "gas expansion parameter," which can also describe gas contraction when the parameter has a negative value, such as it does here.

$$\varepsilon = \left(\sum v_i \right) y_{A,0}$$

$$N_{tot} = N_{tot,0} \left(1 + \varepsilon X_A \right)$$

where $y_{A,0}$ is the initial mole fraction of A. The gas expansion parameter isn't necessary. It just groups terms. I don't bother remembering it. I just remember to check if I have gases, write a stoichiometric table and write the ideal gas law.

The component balance for CO in a batch reactor is

$$\frac{dN_{CO}}{dt} = r_{CO} V$$

For now, consider isothermal reactors, which means T is constant. CO oxidation is an exothermic reaction, so energy has to be removed from the reactor during reaction in order to keep T constant. We will discuss heat transfer and other temperature related (thermal) topics later.

Specify that the reactor volume is constant. This reaction has a change in total moles with conversion. At constant T, a change in total gas moles means that the pressure P will decrease with conversion.

Specify that the ideal gas law applies. We can relate P to X using the ideal gas law

$$PV = N_{tot} RT$$

$$P = N_{tot,0} (1 - 0.5 y_{CO,0} X_{CO}) RT / V$$

$$P = P_0 (1 - 0.5 y_{CO,0} X_{CO}) \quad \text{at constant T and V for ideal gases}$$

More generally, for ideal gases,

$$P = P_0 \left(1 + \left(\sum v_i \right) y_{A,0} X_A \right) \quad \text{at constant T and V}$$

$$\frac{PV}{P_0 V_0} = \frac{N_{tot} RT}{N_{tot,0} R T_0}$$

$$P = P_0 \left(1 + \left(\sum v_i \right) y_{A,0} X_A \right) \left(\frac{T}{T_0} \right) \left(\frac{V_0}{V} \right)$$

Note that we can relate P and X_A to each other using stoichiometry and the ideal gas law. With reaction of gases, it would be easier to measure P and solve for X_A than to measure concentration or partial pressure and solve for X_A

Here is a type of problem you might encounter. Given a constant volume, isothermal batch reactor that is fitted with a pressure gauge. Given an initial P_0 and P at a later time, what is X_A at that later time?

Now what happens when the volume of the reactor changes?

Specify V(t)

First, consider a case where V(t) is specified. This is the case in the cylinder of an internal combustion engine, where V(t) has the approximate shape of a sine wave (not exactly because of the geometry of the piston and connecting rod). Of course, T(t) also changes in that case but let's keep specifying isothermal conditions for now.

The component balance for A becomes

$$\frac{dN_A}{dt} = r_A V(t) \quad \text{where V(t) is known}$$

In the rate equation for r_A , the concentration of any component is given by

$$C_i = \frac{N_i}{V} \quad \text{where, in this case, we have} \quad C_i = \frac{N_i}{V(t)}$$

or by partial pressures, which can also be expressed in terms of $V(t)$. In general, we will need to integrate numerically, updating $V(t)$ at each time step. For isothermal conditions and a power-law rate equation, we will be able to separate variables and may be able to integrate analytically.

Specify constant P

Second, consider a case where the pressure is specified to be constant. With a change in gas moles, the volume will change.

What would a constant pressure batch reactor look like? Maybe a thin, floppy teflon bag in the sun on the roof of the lab so that we can study reactions in synthetic smog. Or maybe we could construct a frictionless sliding piston in a cylinder in the lab.

For our reaction $\text{CO} + 0.5 \text{O}_2 = \text{CO}_2$ let's use the rate equation was discussed in Part 2 on stoichiometry.

$$\frac{dN_{\text{CO}}}{dt} = r_{\text{CO}} V = -k C_{\text{CO}} C_{\text{O}_2} V$$

For a batch reactor, the concentration of any component is given by

$$C_i = \frac{N_i}{V}$$

We could also write the rate equation in terms of partial pressures

$$\frac{dN_{\text{CO}}}{dt} = -k' p_{\text{CO}} p_{\text{O}_2} V$$

$$C_i = \frac{N_i}{V} = \frac{p_i}{RT} \quad ; \quad k' = k / (RT)^2$$

The key thing to do at this point is to realize that V will not be constant. Then double check to make sure we have gases, and then apply the ideal gas law.

$$PV = N_{\text{tot}} RT$$

$$V = N_{\text{tot},0} (1 - 0.5 y_{\text{CO},0} X_{\text{CO}}) RT / P$$

$$V = V_0 (1 - 0.5 y_{\text{CO},0} X_{\text{CO}}) \quad \text{at constant T and P}$$

$$V = V_0 \left(1 + \left(\sum v_i \right) y_{A,0} X_A \right) \quad \text{at constant T and P}$$

So now we have

$$\frac{dN_{CO}}{dt} = -k C_{CO} C_{O_2} V_0 \left(1 + \left(\sum v_i \right) y_{CO,0} X_{CO} \right)$$

$$-N_{CO,0} \frac{dX_{CO}}{dt} = -k \frac{N_{CO}}{V} \frac{N_{O_2}}{V} V$$

$$\frac{dX_{CO}}{dt} = k \frac{N_{CO}}{N_{CO,0}} \frac{N_{O_2}}{V}$$

$$\frac{dX_{CO}}{dt} = k (1 - X_{CO}) \frac{N_{CO,0} (N_{O_2,0} / N_{CO,0} - 0.5 X_{CO})}{V_0 (1 - 0.5 y_{CO,0} X_{CO})}$$

$$\frac{dX_{CO}}{dt} = k (1 - X_{CO}) C_{CO,0} \frac{(N_{O_2,0} / N_{CO,0} - 0.5 X_{CO})}{(1 - 0.5 y_{CO,0} X_{CO})}$$

This can be integrated to solve for X_{CO} vs. t . At any time and conversion, we can compute the volume of the reactor

$$V = V_0 (1 - 0.5 y_{CO,0} X_{CO})$$

The important thing is the process, not these specific equations. Check the following:

- gases?
- constant or variable V ?
- constant or variable P ?
- relatively low P such that we can use ideal gas law?
- write the stoichiometric table
- write the component balance
- continue to work the problem being careful of not making errors if you take short cuts

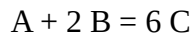
"Spring" reactor

Now let's have some fun. Consider a reactor in which all of the following change: total moles, P , and V .

What would the reactor look like? Maybe reaction of gases inside an elastic balloon. Maybe we can use the sliding piston reactor but connect a spring between the outside of the piston and a wall and also fix the cylinder body.

It might be hard to find a practical example of such a reactor but the problem gives you good practice in learning how to handle complex systems. Here is an example with a cylinder and a piston attached to a spring.

Given:



$$-r_A = k C_A C_B$$

gases, assume ideal gas law applies, constant Temperature

subscript 0 for initial conditions

z is displacement of spring from initial neutral condition, positive z is increasing gas volume

A_x is cross-sectional area of cylinder

K is spring constant

Stoichiometric table

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

$$N_B = N_{B0} - 2N_{A0} X_A$$

$$N_C = 0 + 6N_{A0} X_A$$

$$N_I = 0$$

$$N_{tot} = N_{tot,0} + 3N_{A0} X_A$$

Reactor Equation (component balance for A)

$$\frac{d N_A}{d t} = r_A V = -k C_A C_B V = -k \frac{N_A}{V} \frac{N_B}{V} V$$
$$-N_{A0} \frac{d X_A}{d t} = -k \frac{N_{A0}(1 - X_A) N_{A0} ((N_{B0}/N_{A0}) - 2 X_A)}{V}$$

This term, which is used by Fogler, is optional and adds nothing other than reducing writing:

$$\Theta_B = (N_{B0}/N_{A0})$$

$$\frac{d X_A}{d t} = k \frac{N_{A0}(1 - X_A)((N_{B0}/N_{A0}) - 2 X_A)}{V} = k \frac{N_{A0}(1 - X_A)(\Theta_B - 2 X_A)}{V}$$

We know the following change with time: N_{tot} , V , P . We can use the ideal gas law.

$$PV = N_{tot} RT = (N_{tot,0} + 3 N_{A0} X_A) RT = N_{tot,0} (1 + y_{A0} 3 X_A) RT$$

where y_{A0} is the initial mole fraction of A.

$$PV = N_{tot,0} RT (1 + y_{A0} 3 X_A) = P_0 V_0 (1 + y_{A0} 3 X_A)$$

This term, which is used by Levenspiel and Fogler, is optional and adds nothing other than reducing writing:

$$\varepsilon = y_{A0} \sum v_i = y_{A0} \delta = y_{A0} 3$$

$$PV = P_0 V_0 (1 + y_{A0} 3 X_A) = P_0 V_0 (1 + \varepsilon X_A)$$

The ideal gas law tells us how the product PV changes with conversion. In our other problems, P or V was constant so we then knew how the other variable changed with conversion. Here, however, both P and V change, so we need an additional equation. The pressure and volume are going to be related to how the piston moves. The variable z is a measure of how the piston moves.

We know the relationship between the gas volume and the piston displacement.

$$V = V_0 + A_x z$$

We also know that the gas pressure is balanced by the initial atmospheric pressure plus the pressure exerted by the compressed spring.

$$P = P_0 + \frac{K}{A_x} z$$

Combine the two equations above and do a little rearranging to get

$$(V - V_0) = \left(\frac{A_x^2}{K} \right) (P - P_0)$$

$$P V = \left(P_0 + \frac{K}{A_x} z \right) (V_0 + A_x z) = P_0 V_0 (1 + y_{A0} \beta X_A)$$

$$K z^2 + \left(P_0 A_x + \frac{K V_0}{A_x} \right) z - (P_0 V_0 y_{A0} \beta X_A) = 0$$

Then we would use the quadratic solution formula to solve for z as a function of X_A - the $(-b \pm \sqrt{b^2 - 4ac})/2a$ thing. Choose the real root. For another reaction with a decrease in total moles, z will be negative: the spring stretches and the volume decreases as total moles decrease.

So now we have

$$\frac{dX_A}{dt} = k \frac{N_{A0}(1 - X_A)((N_{B0}/N_{A0}) - 2X_A)}{V_0 + A_x z} \quad \text{where } z = f(X_A)$$

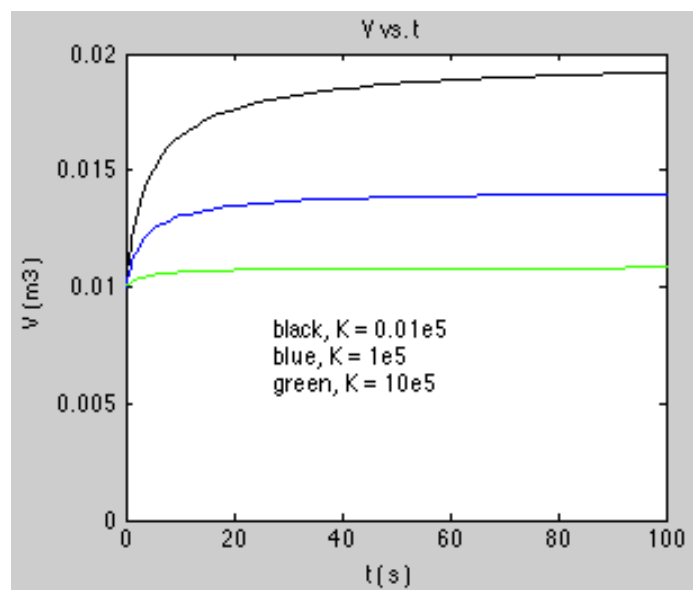
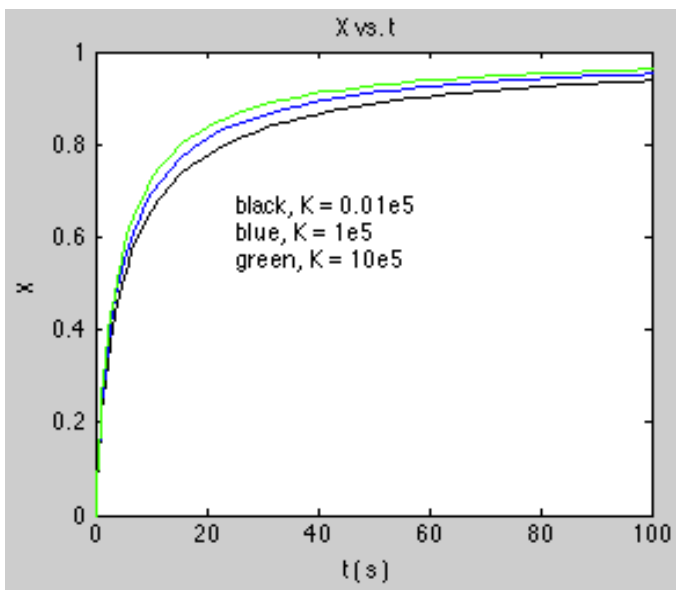
The increase in gas volume and z with reaction tends to reduce the rate of reaction from what it would otherwise be in a constant volume batch reactor.

There are a couple ways to obtain X_A vs. t

1) Levenspiel plot method: separate variables, and compute the inverse rate vs. X_A and then integrate under the curve (math "quadrature") to obtain t vs. X_A .

2) numerically integrate dX_A/dt .

These are plots doing numerical integration. As the value of the spring constant K increases (increasing spring stiffness), the volume change decreases and the rate increases. The rate increases because the reactant concentrations stay higher with smaller increase in volume. At longer time, $X = 1$ is closely approached.



Listing of main m-file

```
% piston and spring reactor
% A + 2 B = 6 C
% -rA = kCACB
% gases, assume ideal gas law applies
% subscript 0 for initial conditions
% constant Temperature
% z is displacement of spring from initial neutral condition,
% positive z is increasing gas volume
% A is cross-sectional area of cylinder
% K is spring constant

P0 = 101.33e3; % Pa
Pa0 = P0/3;
Pb0 = P0 - Pa0;
R = 8.314; % (m3 Pa)/K/mol, ideal gas constant
T = 300; % K, temperature in reactor (constant)
V0 = 0.01; % m3
A = 0.1; % m2, cross sectional area of cylinder
Na0 = Pa0*V0/(R*T);
Nb0 = Pb0*V0/(R*T);

k = 0.01; % (m3/mol/s), rate coefficient
% K (Pa m), spring constant F(Pa m2) = P(Pa) A(m2) = K(Pa-m) z(m)
K = [0.01 1 10] * 1e5;
```



```

X0 = 0; % initial condition, value of initial conversion
tspan = [0 100]; % s, time integration limits
c = ['k' 'b' 'g']; % line colors for plots

for i = 1:3 % step through the different K(i) values

    % integrate dX/dt with std Matlab function ode45
    % derivative in function file springDeriv.m

    % NOTE how the params option of ode45 is used to pass values to ode45,
    % which is better programming practice than using global variables
    params = [P0 V0 A Na0 Nb0 k K(i)]; % inside loop because K(i) changes

    [t X] = ode45('springDeriv',tspan,X0,[],params);
    % results are returned as vectors in [t X]

    % now post-process
    qA = K(i);
    qB = P0*A + K(i)*V0/A;
    qC = -P0*V0*(Na0/(Na0+Nb0))*3*X;
    z = (-qB + sqrt(qB^2 - 4*qA*qC))/(2*qA);
    V = V0 + A*z;

    subplot(2,1,1), plot(t,X,c(i))
    title('X vs. t')
    ylabel('X')
    xlabel('t ( s )')
    hold on
    subplot(2,1,2), plot(t,V,c(i))
    title('V vs. t')
    axis([0 max(t) 0 2*V0])
    ylabel('V ( m3 )')
    xlabel('t ( s )')
    hold on

end

```

Listing of function m-file, springDeriv.m

```

function dXdt = springDeriv(t,X,flags,params)
%
% returns dX/dt for current value of t and X

% parameters are passed in function argument
% alternatively, you can save typing by declaring these variables
% as "global" values but that practice can lead to
% problems in bigger projects, so is not recommended practice

P0 = params(1);
V0 = params(2);
A = params(3);
Na0 = params(4);
Nb0 = params(5);
k = params(6);
K = params(7);

% quadratic equation coefficients for z
qA = K;
qB = P0*A + K*V0/A;
qC = -P0*V0*(Na0/(Na0+Nb0))*3*X;

% use the real root for z
z = (-qB + sqrt(qB^2 - 4*qA*qC))/(2*qA);

dXdt = k*Na0*(1-X)*(Nb0/Na0 - 2*X) / (V0 + A*z);

```