Lecture 17: Volume Changing Reactions

David J. Keffer
Department of Chemical and Biomolecular Engineering
The University of Tennessee, Knoxville
dkeffer@utk.edu
last updated: September 28, 2009

Up to now, we have assumed that the reactions are constant-volume. Now we consider reactions in which the volume may change.

Batch Reactors

1. Reactor, partially filled with liquid where the liquid level rises and falls.
2. gas-phase reaction inside a balloon.

mole balance on A:

$$\frac{dN_A}{dt} = \nu_A r V$$

$$\frac{dN_A}{dt} = \frac{dVC_A}{dt} = C_A \frac{dV}{dt} + V \frac{dC_A}{dt}$$

so we have

$$C_A \frac{dV}{dt} + V \frac{dC_A}{dt} = \nu_A r V$$

We need a volume balance

$$\frac{dV}{dt} = \Delta V_R r V$$

for ideal gas

$$\Delta V_R = \frac{\Delta n_R RT}{p}$$

$$\Delta n_R = \sum_i \nu_i$$

$$\Delta V_R = \frac{RT}{p} \sum_i \nu_i$$

Substitute,

$$C_A \Delta V_R r V + V \frac{dC_A}{dt} = \nu_A r V$$

$$V \frac{dC_A}{dt} = \nu_A r V - C_A \Delta V_R r V = \left(\nu_A - C_A \Delta V_R\right) r V$$

$$\frac{dC_A}{dt} = \left(\nu_A - C_A \Delta V_R\right) r$$

Harder to integrate analytically. Easy to do numerically.

Example:
We consider a gas phase reaction in a batch reactor of variable volume.

The input file is

```
function dydt = sysodeinput(x,y,nvec);
%
% gas-phase batch reactor with variable volume
%
%
%  sample usage:
% [y,x] = sysode(2,1000,0,10000,[20.3121,20.3121,0,10]);
% total initial concentration
%CTin = p/(R*T) = 40.6242 mol/m^3
% initial concentrations of A and B
%CAin = 0.5*CTin = 20.3121 mol/m^3
%CBin = 0.5*CTin
%
CA = y(1);
CB = y(2);
CC = y(3);
V = y(4);
%
%  A + B --> C
%
nuA = -1;
nuB = -1;
nuC = 1;
sumnu = nuA + nuB + nuC;
%
%
%
p = 101325.0; % Pa
```

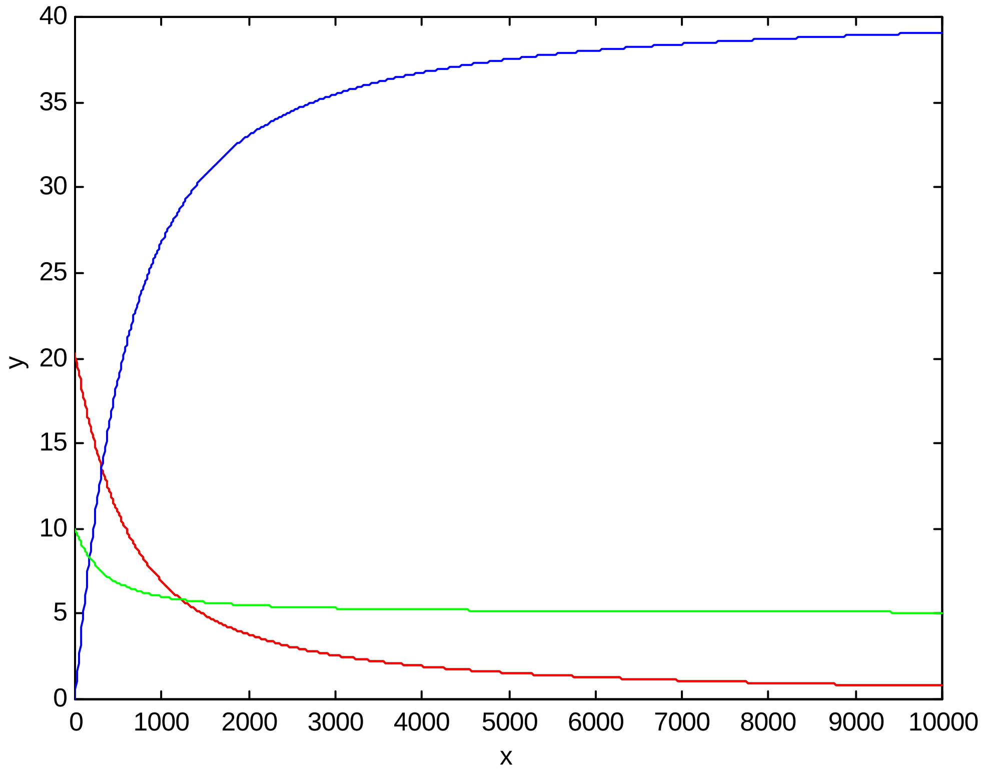
```
R = 8.314; % J/mol/K
T = 300; % K
%
dVR = sumnu*R*T/p; % m^3
ko = 1.0e-3; % m^3/mol/s
Ea = 5000; % J/mol
k = ko*exp(-Ea/(R*T));
rate = k*CA*CB;
%  balance on A in terms of conc of A
dydt(1) = (nuA - CA*dVR)*rate;
%  balance on B in terms of conc of B
dydt(2) = (nuB - CB*dVR)*rate;
%  balance on C in terms of conc of C
dydt(3) = (nuC - CC*dVR)*rate;
%  volume balance
dydt(4) = dVR*rate*V;
```

We type at the command prompt

```
[y,x] = sysode(2,1000,0,10000,[20.3121,20.3121,0,10]);
```

The initial conditions represent the batch reactor initially filled with 50% A and 50% B at 1 bar and T = 300 K. There is no C initially. The initial volume is 10 m^3.

We obtain as an output:



The concentrations of A and B (black and red) overlap and decay with time. The concentration of C (blue) increases in time. The volume of the reactor (green) drops to half its initial value as the extent of reaction moves to 1, since the reaction involves 2 moles of reactant going to 1 mole of product.

Conversion must be based on the number of moles, rather than concentration since the volume changes.

The initial moles of A are

$N_{A,in} = C_{A,in} V_{in}$ moles

The final number of moles is

$N_{A,f} = C_{A,f} V_f$ moles

$$X_A = 1 - \frac{N_{A,f}}{N_{A,in}}$$

CSTR Reactors

1. Reactor, partially filled with liquid where the liquid level rises and falls.
2. Reactor is full and exit flow-rate varies to maintain constant volume.

In general

$$\frac{dVC_A}{dt} = F_{in}C_{A.in} - F_{out}C_A + V\nu_A r$$

$$C_A\frac{dV}{dt} + V\frac{dC_A}{dt} = F_{in}C_{A.in} - F_{out}C_A + V\nu_A r$$

acc = in – out +gen

$$\frac{dV}{dt} = F_{in} - F_{out} + \Delta V_R rV$$

$$V\frac{dC_A}{dt} = F_{in}C_{A.in} - F_{out}C_A + V\nu_A r - C_A\left(F_{in} - F_{out} + \Delta V_R rV\right)$$

$$\frac{dC_A}{dt} = \frac{F_{in}}{V}\left(C_{A.in} - C_A\right) + \left(\nu_A - C_A\Delta V_R\right)r$$

So we see that for a variable-volume CSTR, we get an equation that is analogous to that of the batch reactor.

We can also consider a fixed volume CSTR, in which the reaction changes the number of moles. In this case, we allow the exit flow rate to vary to maintain constant volume

volume balance becomes:

$$\frac{dV}{dt} = 0 = F_{in} - F_{out} + \Delta V_R rV$$

mole balance becomes

$$C_A\frac{dV}{dt} + V\frac{dC_A}{dt} = V\frac{dC_A}{dt} = F_{in}C_{A.in} - F_{out}C_A + V\nu_A r$$

$$\frac{dC_A}{dt} = \frac{F_{in}}{V}C_{A.in} - \frac{F_{out}}{V}C_A + \nu_A r$$

where

$$F_{out} = F_{in} + \Delta V_R r V$$

Again, in a gas, we can use the ideal gas law to get ΔV_R.

Example:

We have a gas-phase reaction in a CSTR where the exit flow-rate fluctuates due to the change in the number of moles in the system.

The input file we used is given below.

```
function dydt = sysodeinput(x,y,nvec);
%
% gas-phase CSTR with variable exit flow-rate
%
%
%  sample usage:
% [y,x] = sysode(2,1000,0,100,[40.6242,0,0]);
% initially tank is filled with A at one atm.
%
CA = y(1);
CB = y(2);
CC = y(3);
%
%  A + B --> C
%
nuA = -1;
nuB = -1;
nuC = 1;
sumnu = nuA + nuB + nuC;
%
%
%
p = 101325.0; % Pa
R = 8.314; % J/mol/K
T = 300; % K
CTin = p/(R*T); % mol/m^3
% initial concentrations of A and B
CAin = 0.4*CTin; % mol/m^3
CBin = 0.6*CTin; % mol/m^3
CCin = 0.0;
%
dVR = sumnu*R*T/p; % m^3
ko = 1.0; % m^3/mol/sec
Ea = 5000; % J/mol
```

```
k = ko*exp(-Ea/(R*T));
rate = k*CA*CB;
%
Fin = 1.0; % m^3/sec
V = 10.0; % m^3;
Fout = Fin + dVR*rate*V;
%
%  molar balances
%
dydt(1) = Fin/V*CAin - Fout/V*CA + nuA*rate;
dydt(2) = Fin/V*CBin - Fout/V*CB + nuB*rate;
dydt(3) = Fin/V*CCin - Fout/V*CC + nuC*rate;
```

At the command line prompt, we typed

```
[y,x] = sysode(2,1000,0,100,[40.6242,0,0]);
```

The initial conditions correspond to the reactor initially filled with A at 1 bar and 300 K.