Experimental Determination of Steady-State and Transient Behavior of Non-Isothermal and Non-Adiabatic Continuous Stirred-Tank Reactors

Extra Credit Project 1: Multiple Steady-States

Computer Project

By

Dr. David Keffer

ChE 301
Department of Chemical Engineering
University of Tennessee
Knoxville, TN
Last Updated: February 2000

Purpose:

This document serves as an appendix to computer project 02. It describes an extra-credit project that can be performed in addition to the mandatory components of computer project 02. This computer project involves using the code written for computer project 02 to describe reactors with multiple steady states.

Multiple Steady-States

The routines that you have used for (a) solution of a system of non-linear algebraic equations and (b) solution of a system of non-linear first-order ordinary differential equations, which describe a chemical reactor can be slightly modified to explore the behavior of the reactor in an infinite variety of situations. One possible avenue of exploration involves reactors with multiple steady states.

Some reactive systems have multiple steady states. Whether you observe multiple steady states depends upon all parameters of the reactor system including inlet conditions, the nature of the reaction, and physical properties. A system that exhibits multiple steady states with a intermediate concentration of reactant in the feed stream may exhibit only a single steady state with low or high concentrations of reactant in the feed stream. The program, sysode.m, can model these systems just as easily as a reactor with a single steady state.

Let’s examine a well-studied reaction from Example 5.4, page 249-250, "Chemical Engineering Kinetics", J.M. Smith, McGraw-Hill, 3rd Edition, New York, 1981. There is one liquid-phase first order irreversible reaction:

$$A \rightarrow D$$

To model this adiabatic system, we can ignore the cooling jacket from computer project 02. An easy way to change the code is to specify that $\dot{Q} = 0.0$.

This system demonstrates 2 stable steady states and one unstable steady state. You should be able to find the steady states using syseqn.m to locate all 3 of the steady state roots. Different initial guesses will lead to different steady states.

You can also locate the 2 stable steady states with sysode.m by following the trajectory in time until it converges to the solution.

The components are labeled reactant A, product D, solvent S, total T.

Using these conditions will yield multiple steady states.

Inlet conditions:

$F_{A,1} = 0.060$ liters/sec

$C_{A,1} = 3.0$ moles/liter

$C_{D,1} = 0.0$ moles/liter

$C_{T,1} = 55.555556$ moles/liter

$C_{S,1} = C_{T,1} - C_{A,1} - C_{D,1}$ moles/liter

$T_1 = 298$ K

Reaction conditions:

$\upsilon_A = 1,\ \upsilon_D = 1.$ (stoichiometric coefficients)

$V = 18$ liters (reactor volume)

$\Delta H_r = 2.09 \cdot 10^5$ J/mole. (exothermic)

$E_a = 62800.0$ J/mole.

$k_o = 4.48 \cdot 10^6 \cdot V$ [1/sec])

Physical properties

$\rho_A = \rho_D = \rho_S = \rho = 1000$ g/liter

$MW_A = MW_D = MW_S = MW = 18$ g/mol

$C_{p,A} = C_{p,D} = C_{p,S} = C_{p,T} = 4.190$ J/g/K

Initial conditions at time = 0

$C_{A,1} = ?$ moles/liter

$C_{D,1} = ?$ moles/liter

$C_{T,1} = 55.555556$ moles/liter

$C_{S,1} = C_{T,1} - C_{A,1} - C_{D,1}$ moles/liter

$T_1 = ?$ K

Use syseqn.m to find the three steady states.

Use sysode.m to map a few trajectories, from different initial conditions.

I have provided some plots of the system below, to help you get started and to give you a feel for whether your results make physical sense. These plots were created by taking the output file from sysode.m, where the concentration and temperature are given as functions of time, and plotting it.

Describe the trajectories you plot with the sysode.m data. You should be able to say something like, for example, “When the initial concentration of the reactant in the reactor is high and the initial temperature is high, the concentration of the reactant drops rapidly to zero, the temperature rises rapidly. Then the temperature slowly decreases to the high-conversion/high-temperature steady state value.”

Appendix one has the a sample input code for sysodeinput.m.

To get you started, this command will give you one trajectory:

```
sysode(2,4000,0,2000,[3,0,52.55555556,373])
```

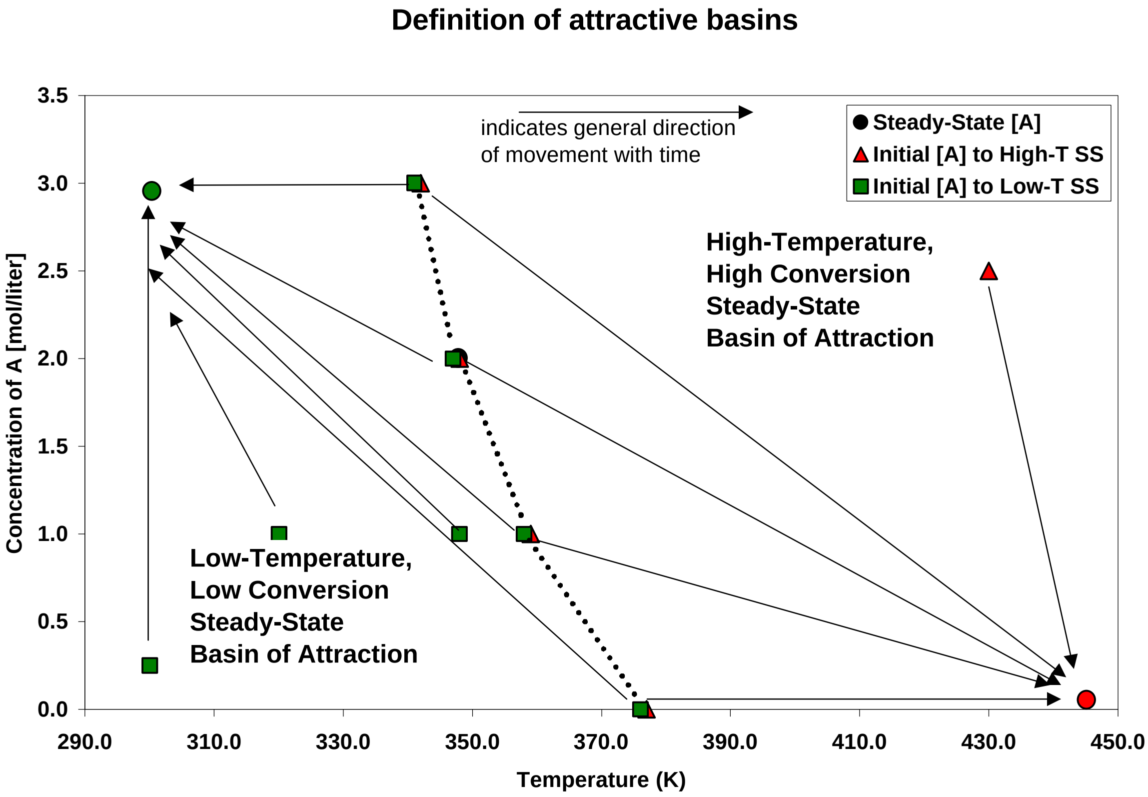

Figure One. In a system with multiple steady states, different initial conditions (concentration and time) yield different steady states. Here, the two circles are two steady states. The triangles are initial conditions that lead to the high temperature, high conversion steady state. The squares are initial conditions that lead to the low temperature, low conversion steady state. The lines with arrows indicate the general direction of the reactor concentration and temperature while moving from the initial condition to the steady state.

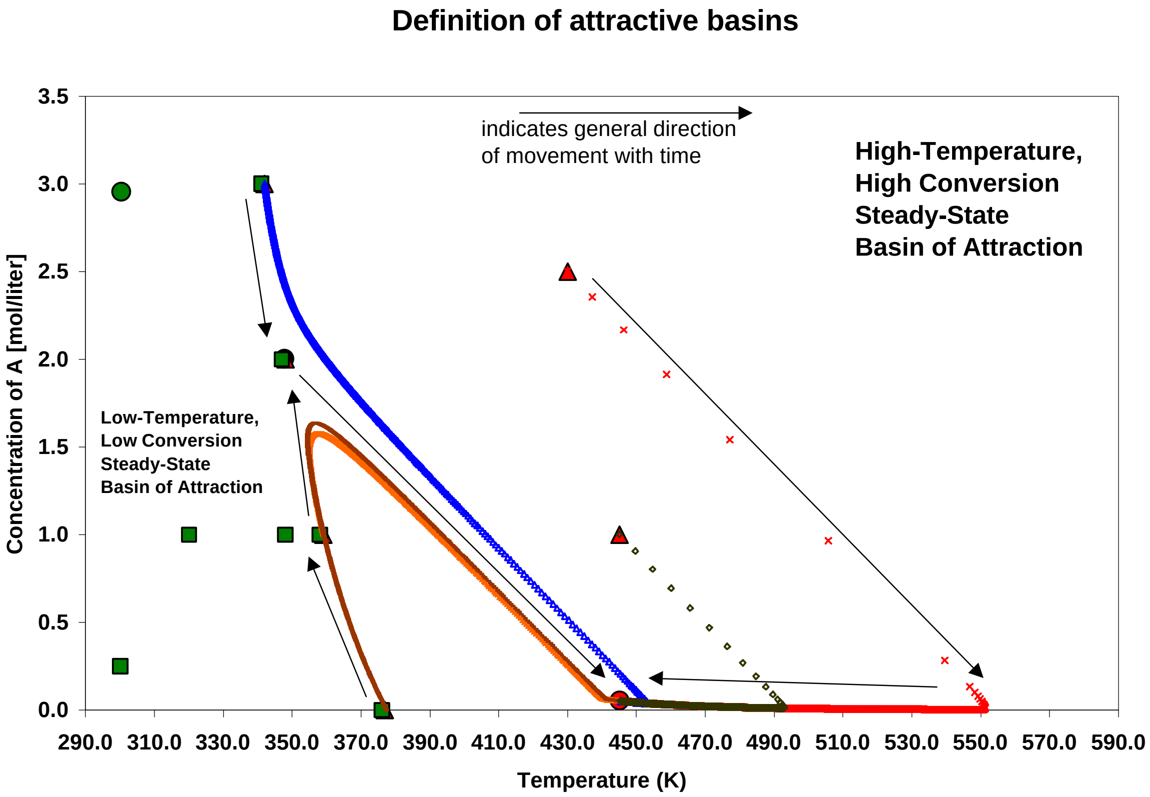

Figure Two. This is the same data as in Figure Three but points have been added which show the actual trajectories (temperature and concentration as a function of time) as the system moves from an initial condition to the high temperature, high conversion steady state.

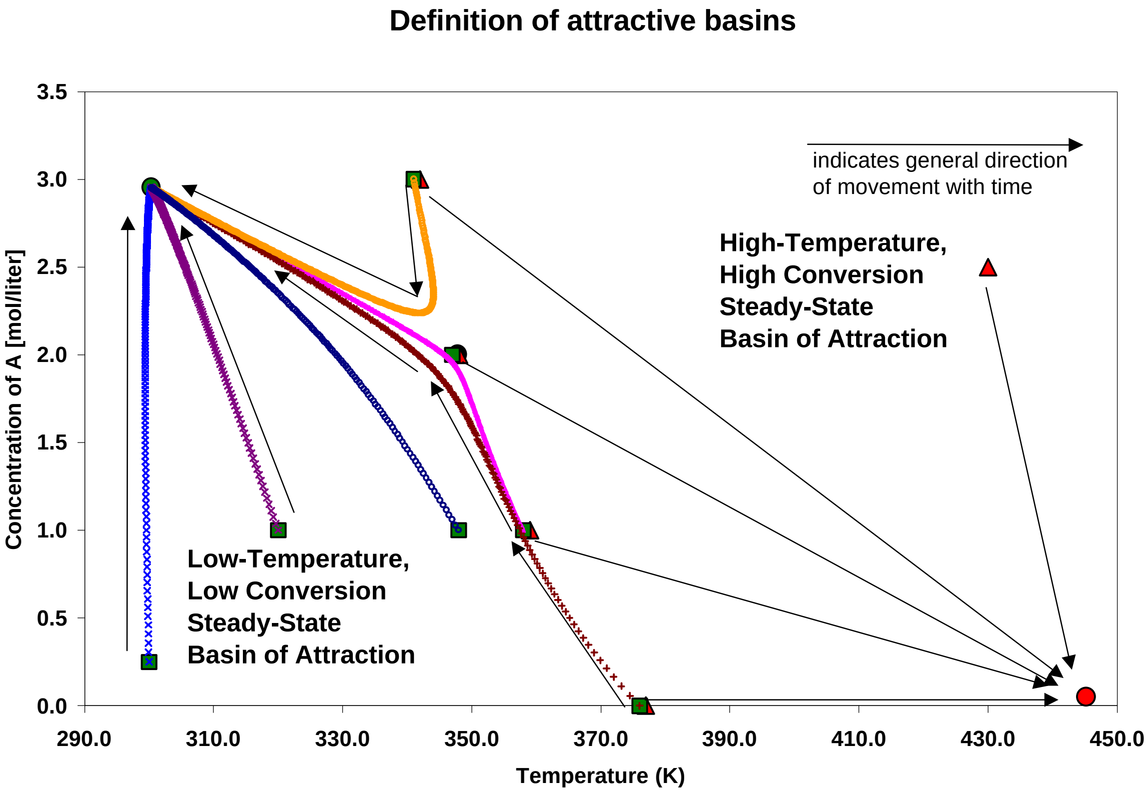

Figure Three. This is the same data as in Figure Three but points have been added which show the actual trajectories (temperature and concentration as a function of time) as the system moves from an initial condition to the low temperature, low conversion steady state.

Appendix One. Sample input file, sysodeinput.m

```
function f = sysodeinput(t,x0,nvec)
%
%  The Data entered here will correspond to the data of
%  Example 5.4, page 249-250, "Chemical Engineering Kinetics",
%  J.M. Smith, McGraw-Hill, 3rd Edition, New York, 1981.
%
%  The system is adiabatic.
%  There is one liquid-phase first order irreversible reaction A-->D
%  initial conditions [CA = 0, CD = 0, CS = 55.5555556, T =  T1]
%
%  An example input
%  sysode(2,4000,0,2000,[3,0,52.55555556,373])
%
%  list the unknown variables
CA = x0(1);
CD = x0(2);
CS = x0(3);
T = x0(4);
%  list the known parameters
%  flowrates in (liters per second)
F1 = 60e-3;
% density rho [grams/liter]
rho = 1000.0;
% molecular weight [grams/mol]
MW = 18.0;
%  inlet Concentrations (mol/liter)
CT = rho/MW;
CA1 = 3.0;
CS1 = CT - CA1;
%  feed temperatures (Kelvin)
T1 = 298;
%  Reactor Volume (liters)
V = 18;
%  Molar Heat Capacities (Joules/mole/Kelvin)
CpA = 4.19*MW;
CpD = 4.19*MW;
CpS = 4.19*MW;
%  Volumetric Enthalpies (Joules/liter)
HE = T*(CpA*CA + CpD*CD + CpS*CS);
H1 = T1*(CpA*CA1 + CpS*CS1);
%  heat input (Joules/sec)
Qdot = 0.0;
%  stoichiometric coefficients
nA = 1;
nD = 1;
%  reaction rate constants
% Gas Constant R [Joules/mol/Kelvin]
R = 8.314;
% ko [1/sec]
ko = 4.48e+6*V;
% Heat of reaciton DHr [Joules/mol]
DHr = 2.09e+5;
% Activation energy Ea [Joules/mol]
Ea = 62800;
rate = (CA^nA)*ko*exp(-Ea/(R*T));
%  isolate the purely algebraic equations
FE = F1 +(nD - nA)*rate/CT;
%  solve for the derivatives
dCAdt = (F1*CA1 - FE*CA - nA*rate)/V;
dCDdt = (-FE*CD + nD*rate)/V;
dCSdt = (F1*CS1 - FE*CS)/V;
num1 = F1*H1 - FE*HE + DHr*rate - Qdot;
num2 = -V*T*(CpA*dCAdt + CpD*dCDdt + CpS*dCSdt);
den = V*(CpA*CA + CpD*CD + CpS*CS);
dTdt = (num1 + num2)/den;
%
f(1) = dCAdt;
f(2) = dCDdt;
f(3) = dCSdt;
f(4) = dTdt;
```