

**Examination of Bifurcations In Reactive Systems  
Cyclical and Chaotic Steady-States**

**Project Statement**

**By**

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## Table of Contents

I. Purpose: .....	1
II. Description of Physical System: .....	1
III. Derivation of Dimensionless Forms of the Equations: .....	2
IV. Parameter Specifications .....	4
V. Problem Assignment .....	4
VI. Numerical Considerations .....	5
Acknowledgements .....	5

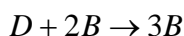
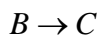
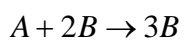
### I. Purpose:

This document is a problem statement for a project on the subject of bifurcations in reactive systems, including the phenomena of period doubling and chaotic behavior.

### II. Description of Physical System:

We consider a continuously stirred tank reactor (CSTR). This reactor has flow in and flow out. The important assumption regarding a CSTR is that the composition of the output stream is the same as that of the reactor contents. In this case, we are concerned only with material balances. We do not consider an energy balance. This essentially assumes that the reactor is operating under isothermal conditions.

Within this reactor, there are three liquid-phase irreversible reactions that take place:



Each of these reactions is elementary so we can write the respective rates of each reaction as

$$r_1 = k_1 C_A C_B^2$$

$$r_2 = k_2 C_B$$

$$r_3 = k_3 C_D C_B^2$$

For any component in the system, the generic material (on a mass or molar basis) balance is given by

$$\textit{accumulation} = \textit{in} - \textit{out} + \textit{generation} - \textit{consumption}$$

where the in and out terms are due to flow and the generation and consumption terms are due to the chemical reactions. For a reactor of volume,  $V$ , we can write balances on the concentration of species  $i$ ,  $C_i$ , as

$$V \frac{dC_i}{dt} = FC_{i,in} - FC_i - k_1 C_A C_B^2$$

where  $N_R$  is the number of reactions in the system and  $\nu_{j,i}$  is the stoichiometric coefficient of component  $i$  in reaction  $j$ , which is negative for reactants and positive for products. For our system, we have four balances

$$V \frac{dC_A}{dt} = FC_{A,in} - FC_A - k_1 C_A C_B^2$$

$$V \frac{dC_B}{dt} = FC_{B,in} - FC_B + k_1 C_A C_B^2 - k_2 C_B + k_3 C_D C_B^2$$

$$V \frac{dC_C}{dt} = FC_{C,in} - FC_C + k_2 C_B$$

$$V \frac{dC_D}{dt} = FC_{D,in} - FC_D - k_3 C_D C_B^2$$

where  $F$  is a volumetric flowrate of the inlet and outlet streams.

### III. Derivation of Dimensionless Forms of the Equations:

We now make this equation dimensionless for ease in solving. We will normalize all concentrations by  $C_{i,in}$  and time by  $V/F$ . Therefore, the dimensionless concentration is

$$C'_i = \frac{C_i}{C_{i,in}} \quad t' = t \frac{F}{V}$$

We eliminate the dimensional variable in terms of the dimensionless variables via direct substitution.

$$FC_{A,in} \frac{dC'_A}{dt'} = FC_{A,in} - FC_{A,in} C'_A - k_1 C_{A,in} C_{B,in}^2 C'_A C'^2_B$$

$$FC_{B,in} \frac{dC'_B}{dt'} = FC_{B,in} - FC_{B,in} C'_B + k_1 C_{B,in}^3 C'_A C'^2_B - k_2 C_{B,in} C'_B + k_3 C_{B,in}^3 C'_D C'^2_B$$

$$FC_{C,in} \frac{dC'_C}{dt'} = FC_{C,in} - FC_{C,in} C'_C + k_2 C_{B,in} C'_B$$

$$FC_{D,in} \frac{dC'_D}{dt'} = FC_{D,in} - FC_{D,in} C'_D - k_3 C_{D,in} C_{B,in}^2 C'_D C_B'^2$$

We divide through the balance for component  $i$  by  $FC_{i,in}$

$$\frac{dC'_A}{dt'} = 1 - C'_A - \frac{k_1 C_{B,in}^2}{F} C'_A C_B'^2$$

$$\frac{dC'_B}{dt'} = 1 - C'_B + \frac{k_1 C_{A,in} C_{B,in}}{F} C'_A C_B'^2 - \frac{k_2}{F} C'_B + \frac{k_3 C_{D,in} C_{B,in}}{F} C'_D C_B'^2$$

$$\frac{dC'_C}{dt'} = 1 - C'_C + \frac{k_2 C_{B,in}}{FC_{C,in}} C'_B$$

$$\frac{dC'_D}{dt'} = 1 - C'_D - \frac{k_3 C_{B,in}^2}{F} C'_D C_B'^2$$

We introduce the following dimensionless quantities. First we have a set of dimensionless ratios of molar feedrates

$$\alpha_i = \frac{\text{molar feedrate of B}}{\text{molar feedrate of i}} = \frac{C_{B,in}}{C_{i,in}}$$

Second, we have a set of Damköhler numbers (ratio of reaction rates to flow rates)

$$D_{a,1} = \frac{k_1 C_{B,in}^2}{F} \quad D_{a,2} = \frac{k_2}{F} \quad D_{a,3} = \frac{k_3 C_{B,in}^2}{F}$$

So that the dimensionless molar balances become

$$\frac{dC'_A}{dt'} = 1 - C'_A - D_{a,1} C'_A C_B'^2$$

$$\frac{dC'_B}{dt'} = 1 - C'_B + D_{a,1} \alpha_A C'_A C_B'^2 - D_{a,2} C'_B + D_{a,3} \alpha_D C'_D C_B'^2$$

$$\frac{dC'_C}{dt'} = 1 - C'_C + D_{a,2}\alpha_C C'_B$$

$$\frac{dC'_D}{dt'} = 1 - C'_D - D_{a,3}C'_D C'^2_B$$

#### IV. Parameter Specifications

For this problem, set the molar ratios to the following values.

$$\alpha_A = 1.5$$

$$\alpha_B = 1.0$$

$$\alpha_C = 0.001$$

$$\alpha_D = 3.50$$

Set the Damköhler numbers to the following values.

$$D_{a,1} = 18000.0;$$

$$D_{a,2} = 80.0;$$

$$D_{a,3} = 400.0;$$

Set the initial conditions to zero. (Assume the reactor is initially full of an unreactive solvent.)

$$C_A = C_B = C_C = C_D = 0.0$$

It's not essential, but your plots will be better scaled if you set the inlet of  $C$  to zero. This can be done simply by setting the in term in the  $C$  balance to zero. If  $C$  is the desired product, it is probably not fed to the reactor.

$$\frac{dC'_C}{dt'} = 0 - C'_C + D_{a,2}\alpha_C C'_B$$

#### V. Problem Assignment

Explore the behavior of the reactor by varying values of  $\alpha_D$ . This change in  $\alpha_D$  corresponds to a decrease in the amount of component D fed to system.

Specifically, include the following six values of  $\alpha_D = 3.5, 3.9, 4.15, 4.18, 4.2, 31$ .

(a) For each value of  $\alpha_D$ , locate the critical point.

- (b) For each value of  $\alpha_D$ , locate the critical point.
- (c) For each value of  $\alpha_D$ , plot the dimensionless concentrations as a function of time.
- (d) For each value of  $\alpha_D$ , generate phase plots that illustrate the relevant behavior of the system.
- (e) Present your results in a professional looking report. Append code (input files) as necessary.

## VI. Numerical Considerations

- (1) Use both techniques for solving systems of nonlinear algebraic equations (e.g. the Newton Raphson method) and for solving systems of ordinary differential equations (e.g. the classical fourth-order Runge-Kutta method) as necessary.
- (2) The maximum allowable step size for your ODE solving routine may vary with  $\alpha_D$ . If your time steps are too big, the algorithm will fail by either providing inaccurate results or crashing.
- (3) The time it takes to reach steady state may vary with  $\alpha_D$ . Solve the ODEs out as long as it takes to clearly identify that a steady state has been reached and what type of state it is.

## Acknowledgements

This problem was first introduced to me by Dr. Jeff Derby at the University of Minnesota in 1995.