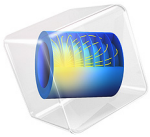

Cubic Autocatalysis: Exploring the Gray–Scott Model

Introduction

An autocatalytic reaction is by definition sped up by its own product. The influence of the product on the rate of the reaction typically means that the reaction is of higher order and therefore nonlinear. For the simple nonlinear model reaction $A + B \rightarrow 2B$, the autocatalysis is said to be ***quadratic***, or to have an overall second reaction order, since it depends on two concentrations, namely those of A and B. In this model, the even more nonlinear cubic case of $A + 2B \rightarrow 3B$ is studied. This model reaction, in the setting of a continuously stirred tank reactor, was the subject of a series of papers in the eighties by the authors Gray and Scott, and their name stuck to the reaction. The authors found that the system exhibited a surprisingly rich set of behaviors, in spite of its compactness. Furthermore, if modeled spatially with competing reaction and diffusion contributions, a mesmerizing evolution of so called Turing patterns, named after the famous British mathematician, occur.

Model Definition

The articles Ref. 1 and Ref. 2, by Gray and Scott, found that a very simple chemical reaction network consisting of one autocatalytic conversion of a substance, and a competing decay of the product, exhibit multistability in the setting of a continuously stirred tank reactor (CSTR):

$$A + 2B \rightarrow 3B \tag{1}$$

$$B \rightarrow \varnothing \tag{2}$$

Not only does the system show multistability, but under certain conditions, the system may become oscillatory. At the critical transitions between two distinct stable states, the systems is exceedingly sensitive to small perturbations in parameter values.

HOMOGENEOUS TREATMENT

As a first step, the reaction system is studied in a 0D component, an external source is given to represent the continuous inflow in the CSTR. The sensitivity is exemplified by a parameter sweep, where the rate coefficient of the first reaction is varied in small steps,

followed by the plotting of the respective results. The parameters used are presented in Table 1.

TABLE 1: PARAMETERS USED IN THE 0D COMPONENT.

NAME	VALUE
k	0.0602/s–0.0603/s
f	0.06/s

The k parameter is swept across 10 equidistant values, to highlight the multistability of the system.

HETEROGENEOUS MODEL

A 2D component describing a square with periodic boundary conditions is generated based on the Reaction Engineering interface. It is known (see Ref. 3) that for a linear reaction system of activator/inhibitor type, instabilities in reaction-diffusion systems can only arise when the diffusion coefficient (divided by its stoichiometric multiplicity) of the activator is less than the corresponding value of the inhibitor. Inspired by this fact for linear systems, substance A is given a diffusion coefficient twice as large as B (see Table 2).

TABLE 2: PARAMETERS USED IN THE 2D COMPONENT.

NAME	VALUE
DA	$2 \cdot 10^{-5}$ m^2/s
DB	$1 \cdot 10^{-5}$ m^2/s

This initial concentrations are inspired by the motifs given in Ref. 5. It should be noted that careful tweaking of the initial conditions is needed for the system to exhibit features such as traveling wavefronts. The k parameters is swept in both cases, and the outcomes are contrasted in line plots and animations, respectively.

The results from the time dependent study for the 0D component is shown in Figure 1.

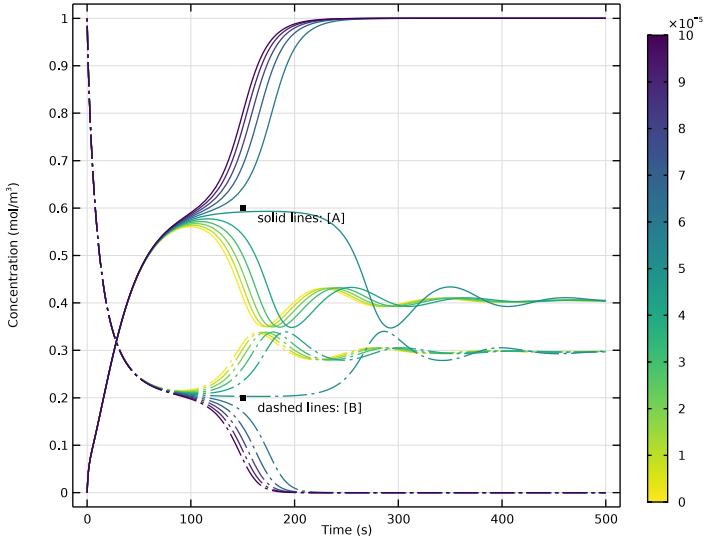

Figure 1: Time evolution of concentration of A and B in the CSTR model for 10 different values of k. The color legend encodes k - 0.0601/s.

Note how the lower five values of k give rise to transitional oscillations into a steady state where both A and B coexist. Whereas the higher five values of k lead to extinction.

The 2D case gives rise to some spectacular Turing patterns (see Ref. 4) for the highest value of k. Check out the end of the modeling instructions on how to use the animation player in COMSOL Multiphysics to view the time evolution of these patterns. It is well worth the effort.

The end state for the run with the highest value of k is shown in Figure 2.

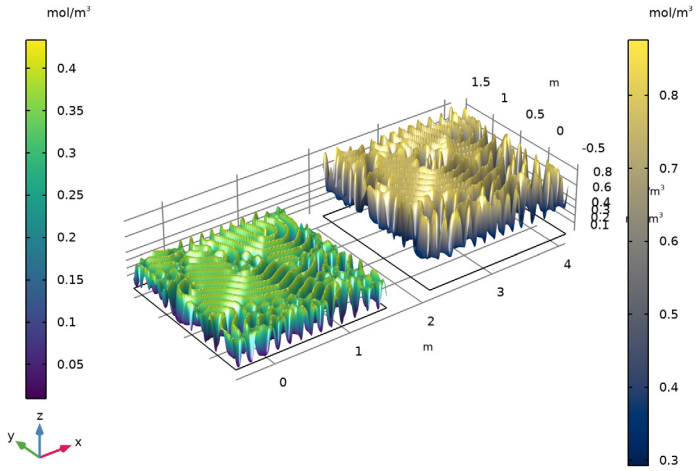

Figure 2: Final state of concentration of A (left) and B (right) for k = 0.06011.

References

1. P. Gray and S.K. Scott, "Autocatalytic Reactions in the Isothermal Continuous Stirred Tank Reactor, Isolas and other forms of multistability," *Chemical Engineering Science*, vol. 38, pp. 29–43, 1983.

2. P. Gray and S.K. Scott, "Autocatalytic Reactions in the Isothermal Continuous Stirred Tank Reactor, Oscillations and instabilities in the system A + 2B=>3B; B=>C," *Chemical Engineering Science*, vol. 39, pp. 1087–1097, 1984.

3. M.C. Cross and P.C. Hohenberg, "Pattern formation outside equilibrium," *Rev. Mod. Phys.*, vol. 65, pp. 851–1112, 1993.

4. A.M. Turing, "The chemical basis of morphogenesis," *Phil. Trans. R. Soc. Lond. B*, vol. 237, pp. 37–72, 1952.

5. R.P. Munafo, "Stable localized moving patterns in the 2-D Gray-Scott model," arXiv:1501.01990 *[nlin.PS]*, 2014.

Application Library path: `Chemical_Reaction_Engineering_Module/Ideal_Tank_Reactors/cubic_autocatalysis`

Modeling Instructions

From the **File** menu, choose **New**.

NEW

In the **New** window, click **Model Wizard**.

MODEL WIZARD

1 In the **Model Wizard** window, click **0D**.

2 In the **Select Physics** tree, select **Chemical Species Transport>Reaction Engineering (re)**.

3 Click **Add**.

4 Click **Study**.

5 In the **Select Study** tree, select **General Studies>Time Dependent**.

6 Click **Done**.

GLOBAL DEFINITIONS

Parameters 1

1 In the **Model Builder** window, under **Global Definitions** click **Parameters 1**.

2 In the **Settings** window for **Parameters**, locate the **Parameters** section.

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `cubic_autocatalysis_parameters.txt`.

REACTION ENGINEERING (RE)

Reaction 1

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Reaction Engineering (re)** and choose **Reaction**.

2 In the **Settings** window for **Reaction**, locate the **Reaction Formula** section.

3 In the **Formula** text field, type `A+2B=>3B`.

Species: B

1 In the **Model Builder** window, click **Species: B**.

2 In the **Settings** window for **Species**, locate the **Chemical Formula** section.

3 Clear the **Enable formula** check box.

Reaction 2

1 In the **Reaction Engineering** toolbar, click **Reaction**.

2 In the **Settings** window for **Reaction**, locate the **Reaction Formula** section.

3 In the **Formula** text field, type `B=>0B`.

4 Locate the **Rate Constants** section. In the k^{f} text field, type `f+k`.

Reaction 3

1 In the **Reaction Engineering** toolbar, click **Reaction**.

2 In the **Settings** window for **Reaction**, locate the **Reaction Formula** section.

3 In the **Formula** text field, type `A=>0A`.

4 Locate the **Rate Constants** section. In the k^{f} text field, type `f`.

Additional Source 1

1 In the **Reaction Engineering** toolbar, click **Additional Source**.

2 In the **Settings** window for **Additional Source**, locate the **Additional Rate Expression** section.

3 In the **Volumetric species** table, enter the following settings:

Species	Additional rate expression (mol/(m^3*s))
A	f

Initial Values 1

1 In the **Model Builder** window, click **Initial Values 1**.

2 In the **Settings** window for **Initial Values**, locate the **Volumetric Species Initial Values** section.

3 In the table, enter the following settings:

Species	Concentration (mol/m^3)
B	1

STUDY 1

Parametric Sweep

1 In the **Study** toolbar, click **Parametric Sweep**.

2 In the **Settings** window for **Parametric Sweep**, locate the **Study Settings** section.

3 Click **Add**.

4 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
k (rate constant)	`range(0.0602, 1e-5, 0.0603)`	`1/s`

Step 1: Time Dependent

1 In the **Model Builder** window, click **Step 1: Time Dependent**.

2 In the **Settings** window for **Time Dependent**, locate the **Study Settings** section.

3 In the **Output times** text field, type `range(0,5,500)`.

4 In the **Study** toolbar, click **Compute**.

RESULTS

Concentration (re)

1 In the **Model Builder** window, expand the **Results>Concentration (re)** node, then click **Concentration (re)**.

2 In the **Settings** window for **1D Plot Group**, click to expand the **Title** section.

3 From the **Title type** list, choose **None**.

Color Expression 1

1 In the **Model Builder** window, right-click **Global 1** and choose **Color Expression**.

2 In the **Settings** window for **Color Expression**, locate the **Expression** section.

3 In the **Expression** text field, type `k-0.0602`.

4 Locate the **Coloring and Style** section. Click **Change Color Table**.

5 In the **Color Table** dialog box, select **Linear>Viridis** in the tree.

6 Click **OK**.

7 In the **Settings** window for **Color Expression**, locate the **Coloring and Style** section.

8 From the **Color table transformation** list, choose **Reverse**.

Global 1

1 In the **Model Builder** window, click **Global 1**.

2 In the **Settings** window for **Global**, locate the **y-Axis Data** section.

3 Click **Clear Table**.

4 In the table, enter the following settings:

Expression	Unit	Description
re.c_A	mol/m^3	Concentration

5 Click to expand the **Legends** section. Clear the **Show legends** check box.

6 Right-click **Global 1** and choose **Duplicate**.

Global 2

1 In the **Model Builder** window, click **Global 2**.

2 In the **Settings** window for **Global**, locate the **y-Axis Data** section.

3 In the table, enter the following settings:

Expression	Unit	Description
re.c_B	mol/m^3	Concentration

4 Click to expand the **Coloring and Style** section. Find the **Line style** subsection. From the **Line** list, choose **Dash-dot**.

Color Expression 1

1 In the **Model Builder** window, expand the **Global 2** node, then click **Color Expression 1**.

2 In the **Settings** window for **Color Expression**, locate the **Coloring and Style** section.

3 Clear the **Color legend** check box.

Annotation 1

1 In the **Model Builder** window, right-click **Concentration (re)** and choose **Annotation**.

2 In the **Settings** window for **Annotation**, locate the **Position** section.

3 In the **x** text field, type `150`.

4 In the **y** text field, type `0.6`.

5 Locate the **Annotation** section. In the **Text** text field, type `solid lines: [A]`.

6 Right-click **Annotation 1** and choose **Duplicate**.

Annotation 2

1 In the **Model Builder** window, click **Annotation 2**.

2 In the **Settings** window for **Annotation**, locate the **Annotation** section.

3 In the **Text** text field, type `dashed lines: [B]`.

4 Locate the **Position** section. In the **y** text field, type `0.2`.

5 In the **Concentration (re)** toolbar, click **Plot**.

This is Figure 1.

REACTION ENGINEERING (RE)

Generate Space-Dependent Model 1

1 In the **Reaction Engineering** toolbar, click **Generate Space-Dependent Model**.

2 In the **Settings** window for **Generate Space-Dependent Model**, locate the **Component Settings** section.

3 From the **Component to use** list, choose **2D: New**.

4 Locate the **Study Type** section. From the **Study type** list, choose **Time dependent**.

5 Locate the **Space-Dependent Model Generation** section. Click **Create/Refresh**.

DEFINITIONS (COMP2)

Variables 1

1 In the **Model Builder** window, expand the **Component 2 (comp2)** node.

2 Right-click **Component 2 (comp2)>Definitions** and choose **Variables**.

3 In the **Settings** window for **Variables**, locate the **Variables** section.

4 Click **Load from File**.

5 Browse to the model's Application Libraries folder and double-click the file `cubic_autocatalysis_variables.txt`.

GEOMETRY 1(2D)

Square 1 (sq1)

1 In the **Model Builder** window, expand the **Component 2 (comp2)** node.

2 Right-click **Component 2 (comp2)>Geometry 1(2D)** and choose **Square**.

3 In the **Settings** window for **Square**, locate the **Size** section.

4 In the **Side length** text field, type `2*l`.

5 Locate the **Position** section. In the **x** text field, type `-l/2`.

6 In the **y** text field, type `-l/2`.

CHEMISTRY 1 (CHEM)

1 In the **Model Builder** window, expand the **Component 2 (comp2)>Chemistry 1 (chem)** node, then click **Chemistry 1 (chem)**.

2 In the **Settings** window for **Chemistry**, click to expand the **Calculate Transport Properties** section.

3 Clear the **Calculate mixture properties** check box.

Species: B

1 In the **Model Builder** window, under **Component 2 (comp2)>Chemistry 1 (chem)** click **Species: B**.

2 In the **Settings** window for **Species**, locate the **Chemical Formula** section.

3 Clear the **Enable formula** check box.

TRANSPORT OF DILUTED SPECIES (TDS)

Initial Values 1

1 In the **Model Builder** window, expand the **Component 2 (comp2)> Transport of Diluted Species (tds)** node, then click **Initial Values 1**.

2 In the **Settings** window for **Initial Values**, locate the **Initial Values** section.

3 In the cA text field, type `cA0`.

4 In the cB text field, type `cB0`.

Periodic Condition 1

1 In the **Physics** toolbar, click **Boundaries** and choose **Periodic Condition**.

2 Select Boundaries 2 and 3 only.

Periodic Condition 2

1 In the **Physics** toolbar, click **Boundaries** and choose **Periodic Condition**.

2 Select Boundaries 1 and 4 only.

Transport Properties 1

1 In the **Model Builder** window, click **Transport Properties 1**.

2 In the **Settings** window for **Transport Properties**, locate the **Diffusion** section.

3 In the D_{cA} text field, type `DA`.

4 In the D_{cB} text field, type `DB`.

MESH 1

Mapped 1

In the **Mesh** toolbar, click **Mapped**.

Distribution 1

1 Right-click **Mapped 1** and choose **Distribution**.

2 In the **Settings** window for **Distribution**, locate the **Distribution** section.

3 In the **Number of elements** text field, type 200.

4 Locate the **Boundary Selection** section. From the **Selection** list, choose **All boundaries**.

5 Click **Build All**.

STUDY 2

Parametric Sweep

1 In the **Study** toolbar, click **Parametric Sweep**.

2 In the **Settings** window for **Parametric Sweep**, locate the **Study Settings** section.

3 Click **Add**.

4 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
k (rate constant)	0.0609 0.06105 0.0611	1/s

5 In the **Study** toolbar, click **Show Default Plots**.

RESULTS

Streamline 1

1 In the **Model Builder** window, expand the **Concentration, A (tds)** node.

2 Right-click **Streamline 1** and choose **Delete**.

Concentration, B (tds)

In the **Model Builder** window, under **Results** right-click **Concentration, B (tds)** and choose **Delete**.

Concentration, A (tds)

1 In the **Model Builder** window, under **Results** click **Concentration, A (tds)**.

2 In the **Settings** window for **2D Plot Group**, click to expand the **Plot Array** section.

3 Select the **Enable** check box.

4 From the **Array shape** list, choose **Square**.

cA

1 In the **Model Builder** window, under **Results>Concentration, A (tds)** click **Surface 1**.

2 In the **Settings** window for **Surface**, type cA in the **Label** text field.

3 Click to expand the **Plot Array** section. Select the **Manual indexing** check box.

4 In the **Column index** text field, type `1`.

Height Expression 1

1 Right-click **cA** and choose **Height Expression**.

2 In the **Settings** window for **Height Expression**, locate the **Axis** section.

3 Select the **Scale factor** check box. In the associated text field, type `1.0`.

cA

1 In the **Model Builder** window, click **cA**.

2 In the **Settings** window for **Surface**, locate the **Coloring and Style** section.

3 Click **Change Color Table**.

4 In the **Color Table** dialog box, select **Linear>Cividis** in the tree.

5 Click **OK**.

6 Right-click **cA** and choose **Duplicate**.

cB

1 In the **Model Builder** window, under **Results>Concentration, A (tds)** click **cA 1**.

2 In the **Settings** window for **Surface**, type `cB` in the **Label** text field.

3 Locate the **Expression** section. In the **Expression** text field, type `cB`.

4 Locate the **Coloring and Style** section. Click **Change Color Table**.

5 In the **Color Table** dialog box, select **Linear>Viridis** in the tree.

6 Click **OK**.

7 In the **Settings** window for **Surface**, locate the **Plot Array** section.

8 In the **Column index** text field, type `0`.

STUDY 2

Step 1: Time Dependent

1 In the **Model Builder** window, under **Study 2** click **Step 1: Time Dependent**.

2 In the **Settings** window for **Time Dependent**, locate the **Study Settings** section.

3 In the **Output times** text field, type `range(0, 1, 10-1) range(10, 10, 300-10) range(300, 100, 1000-100) range(1e3, 1e3, 2e4-1e3) range(2e4, 2.5e3, 5e4-2.5e3) range(5e4, 1e4, 1e5-1e4) range(1e5, 2.5e4, 6e5)`.

4 From the **Tolerance** list, choose **User controlled**.

5 In the **Relative tolerance** text field, type `0.001`.

6 Click to expand the **Results While Solving** section. Select the **Plot** check box.

7 From the **Plot group** list, choose **Concentration, A (tds)**.

8 In the **Study** toolbar, click **Compute**.

RESULTS

Concentration, A (tds)

1 In the **Settings** window for **2D Plot Group**, click to expand the **Title** section.

2 From the **Title type** list, choose **None**.

3 Locate the **Color Legend** section. Select the **Show units** check box.

4 From the **Position** list, choose **Alternating**.

Animation 1

1 In the **Concentration, A (tds)** toolbar, click **Animation** and choose **Player**.

2 In the **Settings** window for **Animation**, locate the **Frames** section.

3 From the **Frame selection** list, choose **All**.

4 Click the **Play** button in the **Graphics** toolbar.

This is Figure 2. Change the animation to show the time evolution corresponding to the intermediate value of k.

5 Locate the **Animation Editing** section. From the **Parameter value (k (1/s))** list, choose **0.06105**.

6 Click the **Play** button in the **Graphics** toolbar.