



Model created in COMSOL Multiphysics 6.4

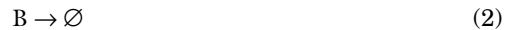
Cubic Autocatalysis: Exploring the Gray–Scott Model

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 continuous stirred tank reactor, was the subject of a series of papers in the 1980s 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 continuous stirred tank reactor (CSTR):



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 system 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	$0.0602/\text{s}-0.0603/\text{s}$
f	$0.06/\text{s}$

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 or 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	$2 \cdot 10^{-5} \text{ m}^2/\text{s}$
DB	$1 \cdot 10^{-5} \text{ m}^2/\text{s}$

These 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.

Results and Discussion

The results from the time-dependent study for the 0D component is shown in [Figure 1](#).

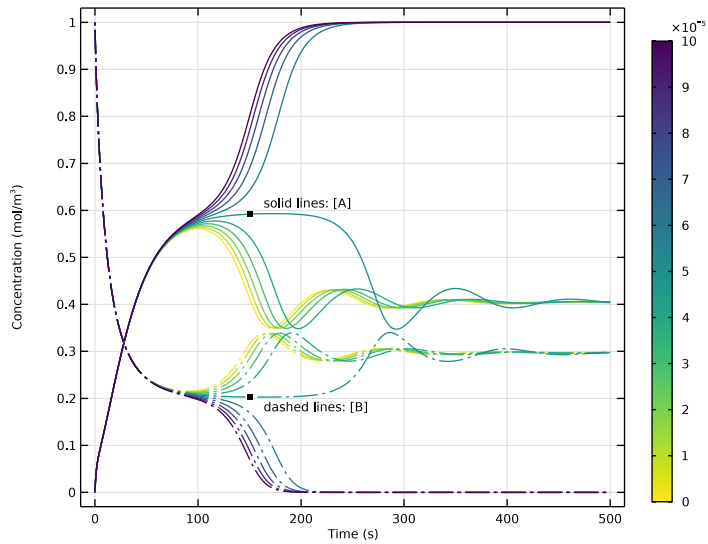


Figure 1: Time evolution of concentration of A and B in the CSTR model for 10 different values of k . The color legend encodes $k - 0.0601/s$.

Notice 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](#).

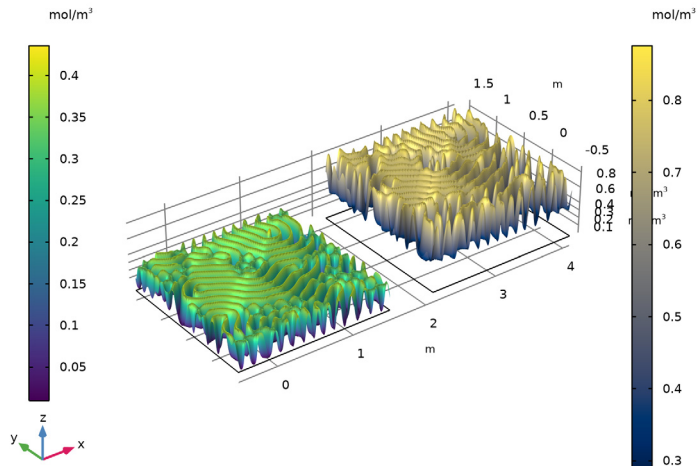


Figure 2: Final state of concentration of A (left) and B (right) for $k = 0.06011$.

References


1. P. Gray and S.K. Scott, “Autocatalytic Reactions in the Isothermal Continuous Stirred Tank Reactor, Isolates 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 $A + 2B \rightarrow 3B$; $B \rightarrow C$,” *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](https://arxiv.org/abs/1501.01990) [*nl.in.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  **OD**.
- 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 **Reaction Engineering** toolbar, click  **Reaction**.
- 2 In the **Settings** window for **Reaction**, locate the **Reaction Formula** section.
- 3 In the **Formula** text field, type $A+2B=>3B$.


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** checkbox.


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 $B \Rightarrow 0B$.
- 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 $A \Rightarrow 0A$.
- 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 I

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 **ID 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. From the **Color table** list, choose **Viridis**.
- 5 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** checkbox.

Global 2

1 Right-click **Results > Concentration (re) > Global 1** and choose **Duplicate**.

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** checkbox.

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 0.593.

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

6 Locate the **Coloring and Style** section. From the **Anchor point** list, choose **Lower left**.

Annotation 2


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

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 0.203.


5 Locate the **Coloring and Style** section. From the **Anchor point** list, choose **Upper left**.

- 6 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 $2*1$.
- 5 Locate the **Position** section. In the **x** text field, type $-1/2$.
- 6 In the **y** text field, type $-1/2$.

CHEMISTRY (CHEM)

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

- 2 In the **Settings** window for **Chemistry**, click to expand the **Calculate Transport Properties** section.
- 3 Clear the **Calculate mixture properties** checkbox.

Species: B

- 1 In the **Model Builder** window, under **Component 2 (comp2) > Chemistry (chem)** click **Species: B**.
- 2 In the **Settings** window for **Species**, locate the **Chemical Formula** section.
- 3 Clear the **Enable formula** checkbox.

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 c_A text field, type c_{A0} .
- 4 In the c_B text field, type c_{B0} .

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.

Fluid 1


- 1 In the **Model Builder** window, click **Fluid 1**.
- 2 In the **Settings** window for **Fluid**, locate the **Diffusion** section.
- 3 In the D_{cA} text field, type D_A .
- 4 In the D_{cB} text field, type D_B .

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

Arrow Surface 1

- 1 In the **Model Builder** window, expand the **Concentration, A (tds)** node.
- 2 Right-click **Arrow Surface 1** and choose **Delete**.

Concentration, B (tds)

In the **Model Builder** window, 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 From the **Array type** 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** checkbox.

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** checkbox. 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 From the **Color table** list, choose **Cividis**.

cB

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

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. From the **Color table** list, choose **Viridis**.

5 Locate the **Plot Array** section. 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** checkbox.

7 In the table, enter the following settings:

Plot group	Plot window
Concentration, A (tds)	Graphics



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** checkbox.
- 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.