

COMSOL REACTION ENGINEERING LAB[®]

USER'S GUIDE

VERSION 1.4

How to contact COMSOL:

Benelux

COMSOL BV
Röntgenlaan 19
2719 DX Zoetermeer
The Netherlands
Phone: +31 (0) 79 363 4230
Fax: +31 (0) 79 361 4212
info@femlab.nl
www.femlab.nl

Denmark

COMSOL A/S
Diplomvej 376
2800 Kgs. Lyngby
Phone: +45 88 70 82 00
Fax: +45 88 70 80 90
info@comsol.dk
www.comsol.dk

Finland

COMSOL OY
Arabianranta 6
FIN-00560 Helsinki
Phone: +358 9 2510 400
Fax: +358 9 2510 4010
info@comsol.fi
www.comsol.fi

France

COMSOL France
WTC, 5 pl. Robert Schuman
F-38000 Grenoble
Phone: +33 (0)4 76 46 49 01
Fax: +33 (0)4 76 46 07 42
info@comsol.fr
www.comsol.fr

Germany

FEMLAB GmbH
Berliner Str. 4
D-37073 Göttingen
Phone: +49-551-99721-0
Fax: +49-551-99721-29
info@femlab.de
www.femlab.de

Italy

COMSOL S.r.l.
Via Vittorio Emanuele II, 22
25122 Brescia
Phone: +39-030-3793800
Fax: +39-030-3793899
info.it@comsol.com
www.it.comsol.com

Norway

COMSOL AS
Søndre gate 7
NO-7485 Trondheim
Phone: +47 73 84 24 00
Fax: +47 73 84 24 01
info@comsol.no
www.comsol.no

Sweden

COMSOL AB
Tegnérsgatan 23
SE-111 40 Stockholm
Phone: +46 8 412 95 00
Fax: +46 8 412 95 10
info@comsol.se
www.comsol.se

Switzerland

FEMLAB GmbH
Technoparkstrasse 1
CH-8005 Zürich
Phone: +41 (0)44 445 2140
Fax: +41 (0)44 445 2141
info@femlab.ch
www.femlab.ch

United Kingdom

COMSOL Ltd.
UH Innovation Centre
College Lane
Hatfield
Hertfordshire AL10 9AB
Phone: +44-(0)-1707 284747
Fax: +44-(0)-1707 284746
info.uk@comsol.com
www.uk.comsol.com

United States

COMSOL, Inc.
1 New England Executive Park
Suite 350
Burlington, MA 01803
Phone: +1-781-273-3322
Fax: +1-781-273-6603

COMSOL, Inc.
10850 Wilshire Boulevard
Suite 800
Los Angeles, CA 90024
Phone: +1-310-441-4800
Fax: +1-310-441-0868

COMSOL, Inc.
744 Cowper Street
Palo Alto, CA 94301
Phone: +1-650-324-9935
Fax: +1-650-324-9936

info@comsol.com
www.comsol.com

For a complete list of international
representatives, visit
www.comsol.com/contact

Company home page

www.comsol.com

COMSOL user forums

www.comsol.com/support/forums

COMSOL Reaction Engineering Lab User's Guide

© COPYRIGHT 1994–2007 by COMSOL AB. All rights reserved

Patent pending

The software described in this document is furnished under a license agreement. The software may be used or copied only under the terms of the license agreement. No part of this manual may be photocopied or reproduced in any form without prior written consent from COMSOL AB.

COMSOL, COMSOL Multiphysics, COMSOL Reaction Engineering Lab, and FEMLAB are registered trademarks of COMSOL AB. COMSOL Script is a trademark of COMSOL AB.

Other product or brand names are trademarks or registered trademarks of their respective holders.

Version: October 2007 COMSOL 3.4

C O N T E N T S

Chapter 1: Introduction

Key Features in Version 1.4	3
Typographical Conventions	3

Chapter 2: Modeling Strategy

Modeling Strategy	6
Perfectly Mixed Reacting Systems: Constant Temperature in Time and Space	9
Perfectly Mixed Reacting Systems: Varying Temperature in Time	15
Space-Dependent Reacting Systems: Varying Temperature in Time	23
Model Validation and Calibration	29
References	47

Chapter 3: The Modeling Environment

Introduction	50
The Model Navigator	53
Model Settings	55
The Batch Reactor	56
The Batch Reactor with Constant Volume	57
The Semibatch Reactor	57
The CSTR with Constant Volume	59
The CSTR with Constant Mass	60
The Plug-Flow Reactor	61
The General Page	64
The Mass Balance Page	65
The Energy Balance Page	67
The Feed Streams Page	68

The Stoichiometry Page	69
The Initial Values Page	72
Reaction Settings—Reactions Interface	73
The Kinetics Page	75
The Thermo Page	79
Reaction Settings—Species Interface	82
The General Page	84
The Feed Stream Page	87
The Thermo Page	89
The Transport Page	95
Constants and Expressions	100
Solver Parameters	102
Parameter Estimation Settings	106
The Data Page	106
The Parameters Page	109
The Advanced Page	111
The Log Page	112
Algorithm for Parameter Estimation	112
Plot Parameters	115
The Solution page	115
The Experimental Data Page	117
Zooming Into the Plots	117
Importing CHEMKIN Files	118
Importing Kinetics Files	119
Kinetic Expressions	121
Supported Keywords	126

Importing Thermodynamics Files	129
Importing Transport Files	133
Importing Experimental Data	135
Exporting Reaction Models	137
Export to Application Modes in the Chemical Engineering Module . . .	137
Export to the COMSOL Script Workspace	143
Exporting Images	144
References	146

Chapter 4: Model Library

Introduction	150
Model Library Guide	150
Degradation of DNA in Plasma	154
Introduction	154
Introduction	154
Model Description	154
Results.	157
Reference	158
Modeling Using COMSOL Script	159
Modeling Using COMSOL Reaction Engineering Lab	160
Drug Release from a Biomaterial	163
Introduction	163
Model Definition	163
Results and Discussion.	167
Reference	169
Modeling Using COMSOL Reaction Engineering Lab	169
Modeling Using COMSOL Multiphysics	176

Enzyme Inhibition Kinetics	180
Introduction	180
Model Description	180
Results.	182
Modeling Using the COMSOL Reaction Engineering Lab	183
 Ozone Combustion	 187
Introduction	187
Model Definition	187
Results.	192
Reference	194
Modeling Using COMSOL Reaction Engineering Lab	195
Modeling Using COMSOL Multiphysics	199
 Diesel Filter	 205
Introduction	205
Model Definition	206
Results.	212
Reference	215
Modeling Using COMSOL Reaction Engineering Lab	216
ID Tubular Reactor	221
Modeling Using COMSOL Multiphysics	224
 Selective Catalytic Reduction of NO_x	 234
Introduction	234
Model Definition	234
Results.	239
Reference	243
Modeling Using the COMSOL Reaction Engineering Lab	244
Modeling Using COMSOL Multiphysics	250
 Homogeneous Charge Compression Ignition of Methane	 258
Introduction	258
Model Definition	258
Results.	262
References	266
Modeling Using the COMSOL Reaction Engineering Lab	266

Pesticide Transport and Reaction in Soil	271
Introduction	271
Model Definition	271
Results.	276
References	279
Modeling Using the COMSOL Reaction Engineering Lab	279
Modeling Using COMSOL Multiphysics	282
 Oscillating Reactions	 289
Introduction	289
Model Descriptions	289
Results.	293
References	296
Modeling Using COMSOL Reaction Engineering Lab	297
Modeling Using COMSOL Script	301
 Analyzing Pressure-Time Data in Parameter Estimation	 305
Introduction	305
Model Definition	305
Results.	307
References	308
Modeling Using the COMSOL Reaction Engineering Lab	309
 Microbial Growth in Food	 312
Introduction	312
Model Description	312
Results.	314
Reference	315
Modeling Using COMSOL Reaction Engineering Lab	315
Modeling Using COMSOL Script	318
 Hydrocarbon Dehalogenation in a Tortuous Microreactor	 320
Introduction	320
Model Definition	320
Results.	324
Modeling Using COMSOL Multiphysics	328
Modeling Using the COMSOL Reaction Engineering Lab	330
Modeling Using COMSOL Multiphysics	333

Ibuprofen Synthesis	336
Introduction	336
Model Description	336
Results.	342
Reference	343
Modeling Using COMSOL Reaction Engineering Lab	344
 Protein Adsorption	 347
Introduction	347
Model Definition	348
Results.	351
Modeling Using COMSOL Reaction Engineering Lab	353
Modeling Using COMSOL Multiphysics	356
 Neutralization of Chlorine in a Scrubber	 359
Introduction	359
Model Definition	359
Results.	361
References	363
Modeling Using COMSOL Reaction Engineering Lab	363
 Non-Isothermal Plug-Flow Reactor	 367
Introduction	367
Model Definition	367
Working with Thermodynamic Polynomials	369
Results.	372
References	375
Modeling Using COMSOL Reaction Engineering Lab	375
 Polymerization in a Semibatch Reactor	 380
Introduction	380
Model Definition	380
Results.	382
Reference	384
Modeling Using COMSOL Reaction Engineering Lab	384
 Startup of a CSTR	 388
Introduction	388

Model Description	388
Results.	391
Reference	393
Modeling Using the COMSOL Reaction Engineering Lab	393
Fluid Catalytic Cracking	399
Introduction	399
Model Description	399
Results.	402
Reference	403
Modeling Using the COMSOL Reaction Engineering Lab	403
Carbon Deposition in Heterogeneous Catalysis	408
Introduction	408
Model Definition	408
Results.	412
References	419
Modeling Using the COMSOL Reaction Engineering Lab	419
Modeling Using COMSOL Multiphysics	422
Kinetics of Pentaerythritol Production	430
Introduction	430
Reaction Kinetics.	430
Mass Balances	431
Evaluating Reaction Rate Parameters From Experimental Data	432
Determining Arrhenius Parameters	434
Results.	435
Reference	437
Modeling Using COMSOL Script	437
Modeling Using COMSOL Reaction Engineering Lab	440
Kinetic Modeling of Cinnamaldehyde Hydrogenation	442
Introduction	442
Model Description	442
Results.	445
Reference	447
Modeling Using the COMSOL Reaction Engineering Lab	448

Chemical Vapor Deposition of GaAs	453
Introduction	453
Introduction	453
Model Definition	453
Results.	459
Reference	463
Modeling Using COMSOL Multiphysics	463
Modeling Using COMSOL Reaction Engineering Lab	465
Modeling Using COMSOL Multiphysics	476

Chapter 5: Reference Section

Variables and Parameters in COMSOL Reaction Engineering Lab	484
Introduction	484
References	494
INDEX	497

Introduction

The COMSOL Reaction Engineering Lab® is a tool that uses reaction formulas to create models of reacting systems. In this context, a model means the material, energy, and momentum balances for a system. The Reaction Engineering Lab not only defines these balances, it can also solve the material and energy balances for space-independent models, that is, for models where the composition and temperature in the reacting system vary only in time. For space-dependent models, the Reaction Engineering Lab offers a direct coupling to the Chemical Engineering Module, the MEMS Module, and the Earth Science Module. This direct link enables you to create models involving material, energy, and momentum balances in COMSOL Multiphysics® directly from a set of reaction formulas.

Included in these models are the kinetic expressions for the reacting system, which are automatically or manually defined in the Reaction Engineering Lab. You also have access to a variety of ready-made expressions in order to calculate a system's thermodynamic and transport properties.

In addition to the formulation and solution of models from reaction formulas, the Reaction Engineering Lab also lets you perform parameter estimation calculations. Using this feature you can readily extract kinetic parameters from experimental data. Furthermore, in combination with COMSOL Script, the Reaction Engineering Lab can implement parametric studies and custom post processing.

We are convinced that the combination of the COMSOL Reaction Engineering Lab, COMSOL Script, and the COMSOL Multiphysics represents the most advanced software for the modeling of reacting systems. Regardless of the system—whether a biological system or a CVD reactor in the semiconductor industry—this suite of products gives you unparalleled power in formulating and solving models.

Key Features in Version 1.4

- Interpretation of reaction formulas entered in the graphical user interface to create the reaction kinetic expressions for a reacting system.
- Formulation of a species list based on entered reaction formulas.
- Formulation and solution of material and energy balances for a set of predefined reactor types; the Batch reactor, the Semibatch reactor, the Continuous stirred tank reactor (CSTR), and the Plug-flow reactor.
- Compilation of thermodynamic and transport properties based on a minimum set of input data.
- Parameter estimation calculations, directly integrated into the graphical user interface.
- Export of simulation data to COMSOL Script for further postprocessing and evaluation.
- Automatic detection of steady state when simulating material and energy balances.
- Export of Reaction Engineering Lab models to COMSOL Multiphysics' Chemical Engineering Module, MEMS Module, and Earth Science Module.
- Import of CHEMKIN[®] files to simulate complex chemical reactions in the gas phase.
- Model Library with 34 entries from various fields that involve chemical reactions.

Typographical Conventions

All COMSOL manuals use a set of consistent typographical conventions that should make it easy for you to follow the discussion, realize what you can expect to see on the screen, and know which data you must enter into various data-entry fields. In particular, you should be aware of these conventions:

- A **boldface** font of the shown size and style indicates that the given word(s) appear exactly that way on the COMSOL graphical user interface (for toolbar buttons in the corresponding tooltip). For instance, we often refer to the **Model Navigator**, which is the window that appears when you start a new modeling session in COMSOL; the corresponding window on the screen has the title **Model Navigator**. As another example, the instructions might say to click the **Multiphysics** button, and the boldface font indicates that you can expect to see a button with that exact label on the COMSOL user interface.

- The names of other items on the graphical user interface that do not have direct labels contain a leading uppercase letter. For instance, we often refer to the Draw toolbar; this vertical bar containing many icons appears on the left side of the user interface during geometry modeling. However, nowhere on the screen will you see the term “Draw” referring to this toolbar (if it were on the screen, we would print it in this manual as the **Draw** menu).
- The symbol > indicates a menu item or an item in a folder in the **Model Navigator**. For example, **Physics>Equation System>Subdomain Settings** is equivalent to: On the **Physics** menu, point to **Equation System** and then click **Subdomain Settings**. **COMSOL Multiphysics>Heat Transfer>Conduction** means: Open the **COMSOL Multiphysics** folder, open the **Heat Transfer** folder, and select **Conduction**.
- A Code (monospace) font indicates keyboard entries in the user interface. You might see an instruction such as “Type 1.25 in the **Current density** edit field.” The monospace font also indicates COMSOL Script codes.
- An *italic* font indicates the introduction of important terminology. Expect to find an explanation in the same paragraph or in the Glossary. The names of books in the COMSOL documentation set also appear using an italic font.

Modeling Strategy

Modeling Strategy

This section describes three primary approaches for using the COMSOL Reaction Engineering Lab in the analysis of a reacting system:

- *Reaction Kinetic Modeling*—During this stage you assume a set of possible variations around a reaction mechanism and then enter them into the Reaction Engineering Lab. You model the mechanism assuming highly controlled conditions in order to compare the simulation to experimental data. These conditions describe the model using one independent variable—generally either time (t) or one space variable (x). You can then perform virtual experiments in the Reaction Engineering Lab to study the influence of various assumptions and conditions on the outcome of the set of reactions. This stage usually involves model calibration, where you tune the model parameters to experimental data. You can find a wide range of functionality for parameter estimation and model calibration in COMSOL Script, which is linked to the Reaction Engineering Lab.
- *Process Modeling*—Here you implement a known or postulated mechanism for a reacting system, defining and modeling it in the Reaction Engineering Lab. You can then design and scale a process, or study the influence of various operating conditions on the process—always assuming that variations in composition and temperature are present only as functions of one independent variable (again, either time or one space variable). Such a process can be any one that involves a reacting system, from the modeling of drug delivery in living tissue to the removal of chlorine in a scrubber tower.
- *Detailed Process Modeling*—During this stage you implement a known mechanism for a reacting system, but here the operating conditions allow for variations in composition and temperature in more than one independent variable, that is, in time and space, or in several space variables (x, y, z). It is therefore interesting to study the influence of these variations on the system's design, for example, different ways to perform mixing in a reactor or the influence of diffusion and convection in drug delivery. In this scenario, you can first set up the system in the Reaction Engineering Lab, which then calculates both the kinetics and the transport properties under ideal conditions. Once the system is properly described under ideal conditions, export your model to the Chemical Engineering Module, MEMS Module, or Earth Science Module of COMSOL Multiphysics, where it is possible to resolve the process given variations in geometry and time.

The modeling strategy in the Reaction Engineering Lab depends on the issues you want to address, as outlined in the three points above. The following discussion provides an introduction to the basic modeling strategy. Later on, this chapter includes a few examples that show the application of the suggested modeling strategies. The three implementation strategies discussed in the following paragraphs correspond to the three approaches just discussed.

- The first and most straightforward modeling scenario deals with perfectly mixed isothermal systems, that is, those with constant temperature in space and time. Here there is no need to compute transport and thermodynamic properties. Under these conditions, the Reaction Engineering Lab does not need information about the system's phase because it treats the system identically for gases and liquids. These conditions are typical for kinetic studies. In such cases, it is desirable to keep temperature strictly controlled, and you can apply mixing to avoid compositional variations, which slow down the interpretation of the experiments.
- In the second scenario, the reacting system is perfectly mixed, but the temperature is not constant over time. Here the Reaction Engineering Lab needs information about the fluid properties. Therefore, the first step in the modeling process is to determine the type of fluid in the reacting system. The second step is to check whether the expressions for energy transport and thermodynamic properties in the Reaction Engineering Lab are appropriate for the system being modeled. For example, the Reaction Engineering Lab contains relevant and accurate functions for properties of gases at low or moderate pressures, and it also provides data for reacting systems that use water as a solvent.
- The third scenario involves the modeling of reacting systems that have substantial variations in composition or temperature as a function of position in the system—an analysis that requires the calculation of energy-transport and material-transport properties. If the variations take place in one space variable at steady state, it might be possible to use the time variable to model the space coordinate. In that case, you can set up and solve the model within the Reaction Engineering Lab. In all other cases, first set up the model and evaluate all transport and thermodynamic properties in the Reaction Engineering Lab; then, after investigating the model's behavior for perfectly mixed conditions, export it to a more extensive model—one that includes the system's geometrical description—for analysis in COMSOL Multiphysics. With this combination of products, the Reaction Engineering Lab can automatically set up the domain equations and the properties of the reacting system in the Chemical Engineering Module, MEMS Module, or Earth Science Module.'

Figure 2-1 provides an overview of the modeling strategy. Without going into great detail, it nonetheless explains the main steps required in setting up a model in the Reaction Engineering Lab.

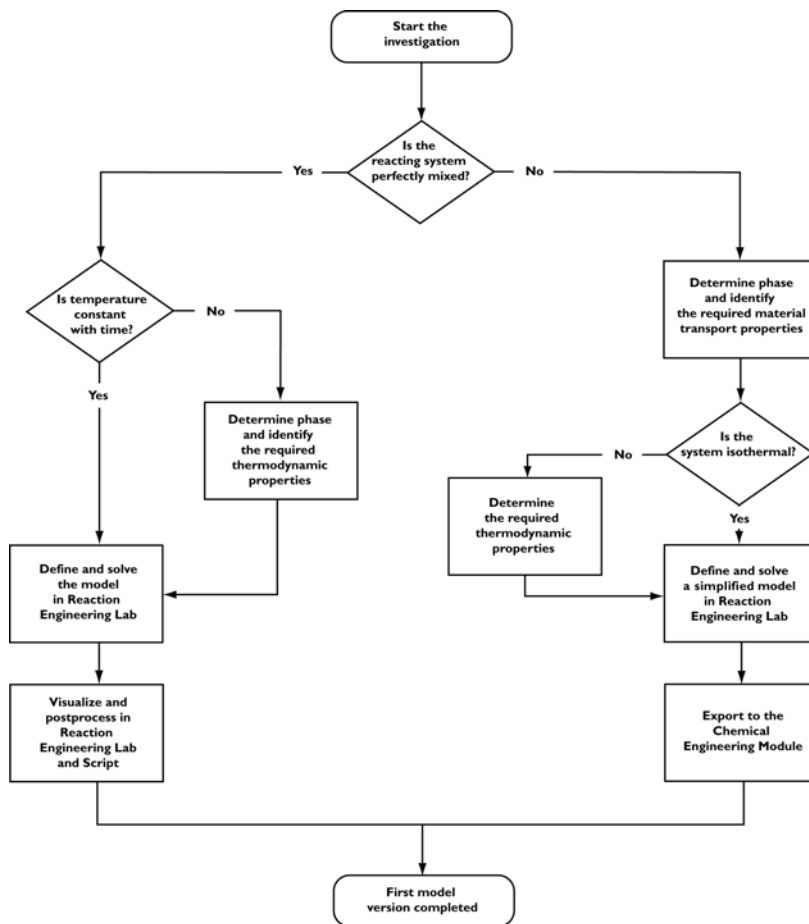


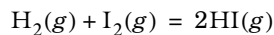
Figure 2-1: Diagram of the strategy for modeling reacting systems in the Reaction Engineering Lab.

The following examples provide details about the implementation of the steps in this figure.

Perfectly Mixed Reacting Systems: Constant Temperature in Time and Space

For a perfectly mixed reactor with a predefined constant temperature, you do not need the reacting system's energy balance in order to describe the system behavior. The behavior is defined as the composition and the production or consumption of species over time. Furthermore, because the reactor is perfectly mixed, the Reaction Engineering Lab can also set up a model even though it has no information about material-transport or energy-transport properties. In this example you make use of Reaction Engineering Labs default reactor type, namely a Batch reactor with constant volume. Other predefined reactor types available are the Semibatch reactor, the Continuous stirred tank reactor (CSTR), and the Plug-flow reactor.

Consider a classical example from the literature on reaction kinetics involving the hydrogen-iodine reaction (Ref. 1). Assume that the bimolecular reaction properly describes the kinetics through the relationship



In a second step, you could also treat the mechanism as suggested by Sullivan (Ref. 1), which involves the equilibrium of the iodine molecule with elementary iodine where both can react with hydrogen to form HI.

For this exercise, simulate an experiment where an equimolar mixture of hydrogen and iodine gas is allowed to react and form HI. The reaction runs under isothermal conditions, and the temperature is kept at 700 K throughout. The experiment takes place in a perfectly mixed batch reactor.

The purpose of the experiment is to study the composition in the reactor over time and determine how long it takes the system to reach steady state, where it is possible to determine the reaction's equilibrium constant.

Under these conditions, the modeling procedure in the Reaction Engineering Lab is:

- 1 Start the Reaction Engineering Lab.
- 2 Set the system temperature.
- 3 Set a new reaction and enter the expression for the reaction as just given.
- 4 Set the initial concentrations of H_2 , I_2 , and HI.
- 5 Set the time interval for the reactor simulation.
- 6 Compute the solution.

7 Plot the solution.

The input data consists of the following:

- Frequency factor for the forward reaction $A_f = 8.87 \cdot 10^7 \text{ m}^3/(\text{mol} \cdot \text{s})$.
- Frequency factor for the reverse reaction $A_r = 3.00 \cdot 10^7 \text{ m}^3/(\text{mol} \cdot \text{s})$.
- Activation energy for the forward reaction $E_f = 167 \cdot 10^3 \text{ J/mol}$.
- Activation energy for the reverse reaction $E_r = 184 \cdot 10^3 \text{ J/mol}$.
- Initial concentration for both H_2 and $\text{I}_2 = 8.71 \text{ mol/m}^3$.
- System temperature = 700 K.

Model Library path: Education/isothermal_hi_reactor

The following instructions show the detailed implementation of the model as just sketched.

MODELING IN THE REACTION ENGINEERING LAB

Defining the Reactions

- 1 Double-click the Reaction Engineering Lab icon on the desktop to open the **Model Navigator**.
- 2 Click the **New** button. The main user interface window should now be active.
- 3 Go to the **Model** menu and select **Model Settings**. In the **Temperature** edit field, type 700. Click **Close**.
- 4 From the **Model** menu, select **Reaction settings**. Click the **New** button.
- 5 Find the **Formula** edit field and type $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$. Press the Enter key.

- 6 Select the **Use Arrhenius expressions** check box. The **Reaction settings** dialog box should now look like this:

Reaction Settings

Reactions Species

Reaction selection

1: H2+I2<=>2HI

Formula

H2+I2<=>2HI Type: Reversible

Kinetics Thermo

☒ Use Arrhenius expressions

Arrhenius parameters

Quantity	Value/Expression		Unit	Description
	forward	reverse		
A	1	1		Frequency factor
n	0	0		Temperature exponent
E	0	0	J/mol	Activation energy

Kinetic expressions

Quantity	Value/Expression	Unit	Description
k_f^r	1		Forward rate constant
k_r^r	1		Reverse rate constant

☐ Specify equilibrium constant

k_0^{eq}	1		Equilibrium constant
k^{eq}	0		Equilibrium expression
r	$k_f_1*c_{H2}*c_{I2}-l_r_1*c_{HI}^2$	mol/(m ³ -s)	Reaction rate

New Delete Reset Close Help

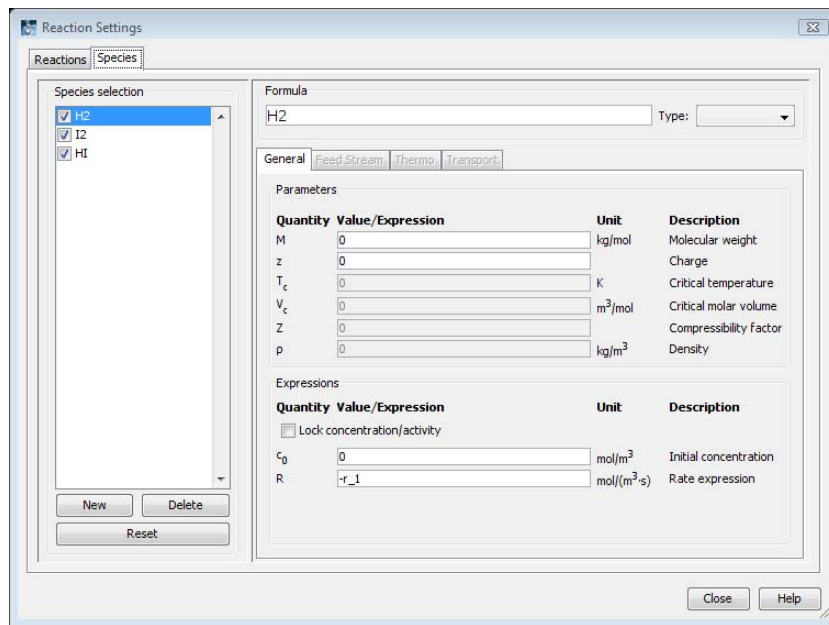
Note that the delimiter **<=>** defines a reversible reaction. In contrast, the delimiter for an irreversible reaction is either **=>** or **<=**, and an equilibrium reaction is specified with the **=** symbol. Note also that the Reaction Engineering Lab automatically sets the reaction rate expression using the mass action law and puts the result in the corresponding **Reaction rate** edit field.

- 7 Go to the **Arrhenius parameters** area. Find the column for the **forward** reaction. Go to the **A** edit field for the **Frequency factor** and type **8.87e7**, then in the **E** edit field for the **Activation energy** type **167e3**.
- 8 Find the column for the **reverse** reaction. Go to the **A** edit field for the **Frequency factor** and type **3.00e7**, then in the **E** edit field for the **Activation energy** type **184e3**.

The Species Selection List

- 1 Click the **Species** tab to examine the **Species selection** list and the corresponding material balances for each species. The Reaction Engineering Lab creates the **Species selection** list automatically as you type in the reaction.

- Click on species **H2** in the **Species selection** list. The user interface should look like this:



- Locate the **c₀** edit field for the initial concentration of species **H₂** and type **8.71**. Doing so sets the initial concentration in mol/m³.
- Click **I2** in the **Species selection** list and set the **Initial concentration** to **8.71 mol/m³**.
- Check that the initial concentration of **HI** is set to 0. Click **Close**.

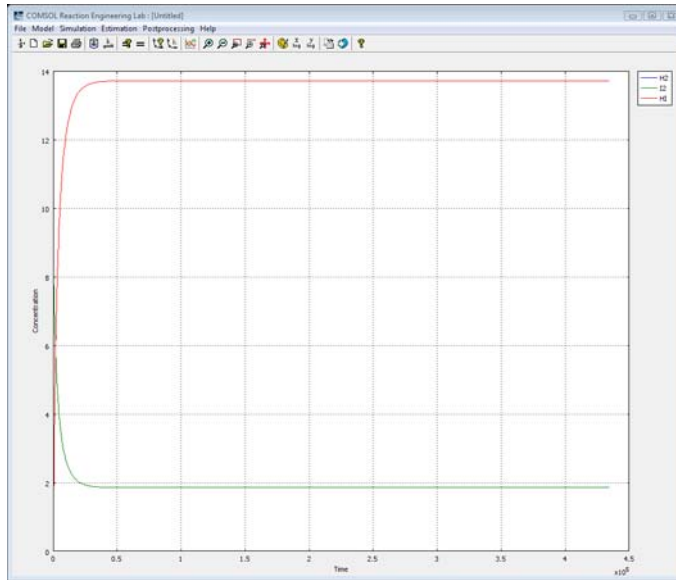
Computing the Solution

Click the **Solve Problem** button (=) on the Main toolbar.

Reaction Engineering Lab uses an internal stop condition for the simulation time. The time stepping stops when the material balances have reached steady state according to the tolerance that you can specify in the **Solver Parameters** dialog box. In this case, the default settings cause the solver to stop at $3.4 \cdot 10^5$ seconds. The resulting plot shows that the transients are captured using the default settings.

Plotting the Solution

The Reaction Engineering Lab automatically displays the concentration of reactants and products as shown in the following figure:



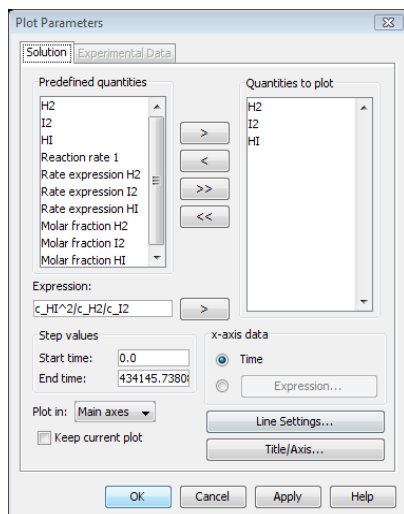
This plot shows that the reactor is close to steady state after roughly 36,000 s (10 hours). It is therefore interesting to check the value of the relationship

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

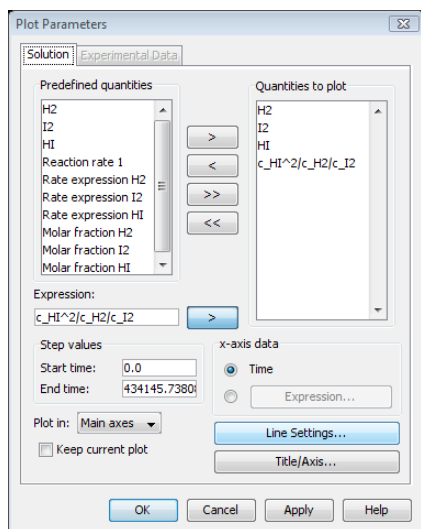
which at steady state, in this case, should yield the equilibrium constant. The following steps show how to define and plot the equilibrium expression:

- 1 From the **Postprocessing** menu, select **Plot Parameters**.
- 2 In the **Expression** edit field, type $c_{\text{HI}}^2/c_{\text{H}_2}/c_{\text{I}_2}$, which is the equilibrium expression.
- 3 Click the **Add Entered Expression** button (>).

4 Type 57600 in the **End time** edit field in the **Time values** area.



5 Click **OK**.

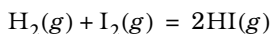


The resulting plot shows that the equilibrium expression asymptotically reaches the value of roughly 54.9 (dimensionless), which is also the relationship between k^f and k^r in the model.

Perfectly Mixed Reacting Systems: Varying Temperature in Time

In the case of a perfectly mixed nonisothermal system, you have to set up both the time-dependent material and energy balances. There are no spatial concentration gradients because the system is perfectly mixed, so the Reaction Engineering Lab can create a model without evaluating the material-transport properties.

Returning to the previous example, continue with the formation of HI described by the reaction



The energy balance for the Batch reactor is by default defined according to the equation

$$V_r \sum_i c_i C_{p,i} \frac{dT}{dt} = w_s + Q + Q_{\text{ext}} + V_r \frac{dp}{dt}$$

In the above equation V_r denotes the system volume (m^3), c_i is the species concentration (mol/m^3), $C_{p,i}$ is the species molar heat capacity ($\text{J}/(\text{mol}\cdot\text{K})$), T is the temperature (K), and p the pressure (Pa). On the right hand side, w_s represents the shaft work (J/s), Q is the heat due to chemical reaction (J/s), and Q_{ext} denotes heat added to the system (J/s). The heat of reaction is given as:

$$Q = -V_r \sum_j H_j r_j$$

For this scenario, the modeling procedure in the Reaction Engineering Lab is:

- 1 Start the Reaction Engineering Lab.
- 2 Select the type of fluid (gas) and activate the energy balance.
- 3 Set a new reaction and type in the expression for the reaction just described.
- 4 Set the initial concentrations for H_2 , I_2 , and HI .
- 5 Set the thermodynamic properties of H_2 , I_2 , and HI .
- 6 Set the time interval for the reactor simulation.
- 7 Compute the solution.
- 8 Plot the solution.

At this stage, include the polynomials that describe the heat capacity, $C_{p,i}$, for each species i as input data to the model. In addition you need the enthalpy of formation

and the entropy of formation at 0 K for each of the three species. These are usually tabulated in NASA polynomial files for thermodynamic properties of pure gases.

The following list summarizes the input data for the model:

- Frequency factor for the forward reaction $A_f = 8.87 \cdot 10^7 \text{ m}^3/(\text{mol} \cdot \text{s})$
- Frequency factor for the reverse reaction $A_r = 3.00 \cdot 10^7 \text{ m}^3/(\text{mol} \cdot \text{s})$
- Activation energy for the forward reaction $E_f = 167 \cdot 10^3 \text{ J/mol}$
- Activation energy for the reverse reaction $E_r = 184 \cdot 10^3 \text{ J/mol}$
- Initial concentration for both H_2 and $\text{I}_2 = 8.71 \text{ mol/m}^3$
- Initial system temperature = 700 K

The polynomials for C_p ($\text{J}/(\text{mol} \cdot \text{K})$) are arranged according to the expression

$$\frac{C_p}{R_g} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

and their coefficients take on the following values:

TABLE 2-1: COEFFICIENT VALUES FOR VARYING TEMPERATURE

	a_1	a_2	a_3	a_4	a_5	$h_{0,0K}/R_g$	$s_{0,0K}/R_g$
H_2	2.883	$3.681 \cdot 10^{-3}$	$-7.720 \cdot 10^{-6}$	$6.920 \cdot 10^{-9}$	$-2.130 \cdot 10^{-12}$	$-9.671 \cdot 10^2$	-1.034
I_2	3.508	$6.303 \cdot 10^{-3}$	$-1.461 \cdot 10^{-5}$	$1.470 \cdot 10^{-8}$	$-5.310 \cdot 10^{-12}$	$6.287 \cdot 10^3$	$1.002 \cdot 10^1$
HI	3.648	$-1.392 \cdot 10^{-3}$	$3.890 \cdot 10^{-6}$	$-3.260 \cdot 10^{-9}$	$1.100 \cdot 10^{-12}$	$2.131 \cdot 10^3$	4.334

Note that $h_{0,0K}$ and $s_{0,0K}$ are fictitious enthalpies and entropies calculated as

$$h_{0,0K} = h_{0,298K} + \int_{298}^0 C_p dT$$

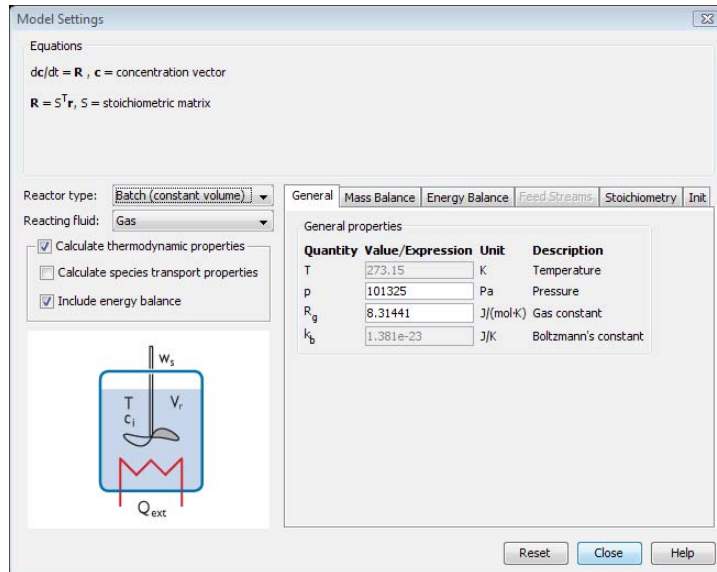
The equation uses the C_p polynomials in the integral expression despite the fact that these might not be valid all the way down to 0 K. This inclusion does not introduce an error, because contributions outside the interval are cancelled out in every integration in the non-isothermal system (when going from T_1 to T_2) as long as the system temperature is within the correct interval. To calculate the entropy, follow the a procedure for $s_{0,0K}$ analogous to the one described earlier for $h_{0,0K}$. This is also a standard way of calculating $s_{0,0K}$ and $h_{0,0K}$ in NASA polynomials for thermodynamic data.

Model Library path: Education/nonisothermal_hi_reactor

MODELING IN THE REACTION ENGINEERING LAB

Defining the Reactions

- 1 Start the Reaction Engineering Lab to open the **Model Navigator**.
- 2 Click the **New** button.
- 3 Go to the **Model** menu and select **Model Settings**.
- 4 Select the **Calculate thermodynamic properties** and **Include energy balance** check boxes.
- 5 The dialog box should look like this:



- 6 Click **Close**.
- 7 Click the **Reaction settings** button on the Main toolbar.
- 8 Click the **New** button in the lower-left corner in the **Reactions** page.
- 9 Go to the **Formula** edit field and type H2+I2<=>2HI, then press the Enter key.
- 10 Select the **Use Arrhenius expressions** check box.

11 Go to the **Arrhenius parameters** area. Find the column for the **forward** reaction. In the **A** edit field for the **Frequency factor** type 8.87e7, then in the **E** edit field for the **Activation energy** type 167e3.

12 Locate the column for the **reverse** reaction. In the **A** edit field for the **Frequency factor** type 3.00e7, then in the **E** edit field for **Activation energy** type 184e3.

The Species Selection List

- 1 Click the **Species** tab to review the **Species selection** list and the corresponding material balances for each species. Click on species **H2**, then in the **c₀** edit field for the **Initial concentration** type 8.71.
- 2 Click the **Thermo** tab. Enter the appropriate numbers in the first row (corresponding to H₂ in Table 2-1) in the edit fields labeled **a_{low,k}**. To use the same polynomials for the entire temperature interval, type 50 in the **lower** edit field for the **Temperature interval limits**, then type 3000 in the **midpoint** and **upper** edit fields. When you click on either of the **Polynomial coefficients** edit fields a table appears, and its rows are ordered identically to the input data listed in Table 2-1: a_1 , a_2 , a_3 , a_4 , a_5 , $h_{0,0K}/R_g$, and $s_{0,0K}/R_g$. The user interface should look like this when you click on the **Polynomial coefficients** edit field:

The screenshot shows the 'Reaction Settings' dialog box with the 'Species' tab selected. On the left, the 'Species selection' list includes H2, I2, and HI, all of which are checked. Below this list are 'New', 'Delete', and 'Reset' buttons. The main area of the dialog is divided into several sections. At the top, the 'Formula' field contains 'H2' and the 'Type' dropdown is set to 'Gas'. Below this, the 'Thermo' tab is active, displaying 'Thermodynamic parameters' and 'Thermodynamic expressions'.

Thermodynamic parameters

Quantity	Value/Expression	Unit	Description
T _{int}	lower: 50, midpoint: 3000, upper: 3000	K	Temperature interval limits
a _{low,k}	2.883 3.681E-03 -7.720E-06 6.92		Polynomial coefficients
a _{hi,k}	0 0 0 0 0 0		Polynomial coefficients

Thermodynamic expressions

Quantity	Value/Expression	Unit	Description
s	Rg*((T<=Tlo_H2)*(aLo1_H2*log	J/(mol·K)	Molar entropy
h	Rg*((T<=Tlo_H2)*Tlo_H2*(aLo1	J/mol	Molar enthalpy
C _p	Rg*((T<=Tlo_H2)*(aLo1_H2+aLc	J/(mol·K)	Heat capacity at constant pressure

At the bottom right of the dialog are 'Close' and 'Help' buttons.

- 3 Click the **General** tab.

- 4 In the **Species selection** list click **I2**, then in the **c₀** edit field for the initial concentration type 8.71.
- 5 Click the **Thermo** tab and set the **Temperature interval limits**: type 50 in the **lower** edit field, 3000 in the **midpoint** edit field, and 3000 in the **upper** edit field.
- 6 Enter values in the **a_{low,k}** **Polynomial coefficients** edit fields, which corresponds to I₂ in Table 2-1:

Reaction Settings

Reactions Species

Species selection

- ☒ H2
- ☒ I2
- ☒ HI

New Delete Reset

Formula: I2 Type: [v]

General Feed Stream Thermo Transport

Thermodynamic parameters

Quantity	Value/Expression	Unit	Description
T _{int}	lower: 50 midpoint: 3000 upper: 3000	K	Temperature interval limits
a _{low,k}	3.508 6.303E-03 -1.461E-05 1.47		Polynomial coefficients
a _{hi,k}	0 0 0 0 0		Polynomial coefficients

Thermodynamic expressions

Quantity	Value/Expression	Unit	Description
s	Rg*((T<=Tlo_I2)*(aLo1_I2*log(T	J/(mol-K)	Molar entropy
h	Rg*((T<=Tlo_I2)*Tlo_I2*(aLo1_I	J/mol	Molar enthalpy
C _p	Rg*((T<=Tlo_I2)*(aLo1_I2+aLo2	J/(mol-K)	Heat capacity at constant pressure

Close Help

- 7 Click the **General** tab.
- 8 In the **Species selection** list click on **HI**, then in the **c₀** edit field for the initial concentration, make sure that the value is set to 0 (this is the default value).

- 9 Click the **Thermo** tab and specify the **Temperature interval limits** according to those already mentioned. Enter values in the lower **Polynomial coefficient**, $a_{low,k}$, edit field corresponding to HI in Table 2-1. Click **Close**.

Reaction Settings

Reactions Species

Species selection

- ☒ H2
- ☒ I2
- ☒ HI

Formula: HI Type: [dropdown]

General Feed Stream Thermo Transport

Thermodynamic parameters

Quantity	Value/Expression			Unit	Description
	lower	midpoint	upper		
T_{int}	50	3000	3000	K	Temperature interval limits
$a_{low,k}$	3.648	-1.392E-03	3.890E-06	-3.2	Polynomial coefficients
$a_{hi,k}$	0	0	0	0	Polynomial coefficients

Thermodynamic expressions

Quantity	Value/Expression	Unit	Description
s	$Rg*((T<=Tlo_HI)*(a_{lo1_HI}*log(\dots))$	J/(mol*K)	Molar entropy
h	$Rg*((T<=Tlo_HI)*Tlo_HI*(a_{lo1_HI} + \dots)$	J/mol	Molar enthalpy
C_p	$Rg*((T<=Tlo_HI)*(a_{lo1_HI} + a_{lo1_HI} + \dots)$	J/(mol*K)	Heat capacity at constant pressure

New Delete Reset

Close Help

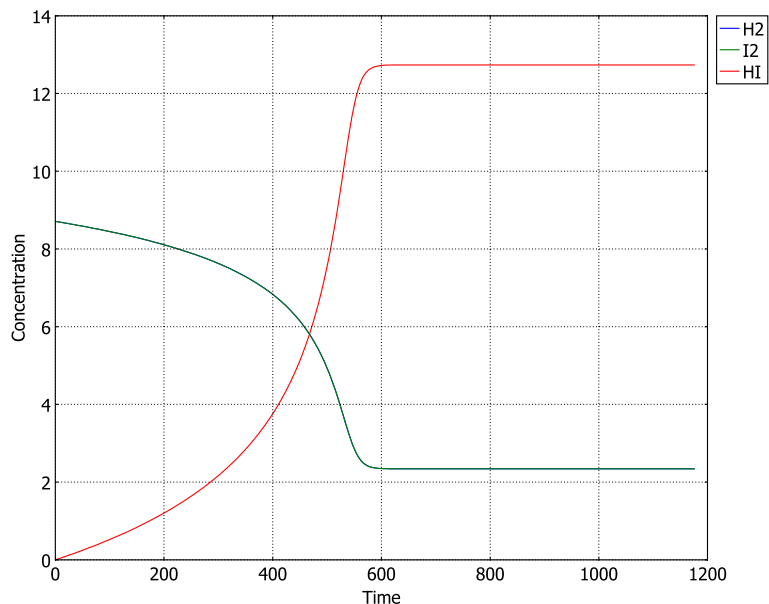
Setting the Simulation Parameters and Computing the Solution

- 1 From the **Model** menu, select **Model Settings**.
- 2 Select the **Init** page.
- 3 In the $T(t_0)$ edit field for **Initial temperature**, type 700. Click **Close**.
- 4 Click the **Solve Problem** button (=) on the Main menu.

Reaction Engineering Lab stops the simulation at approximately 950 seconds, where the system reaches steady state.

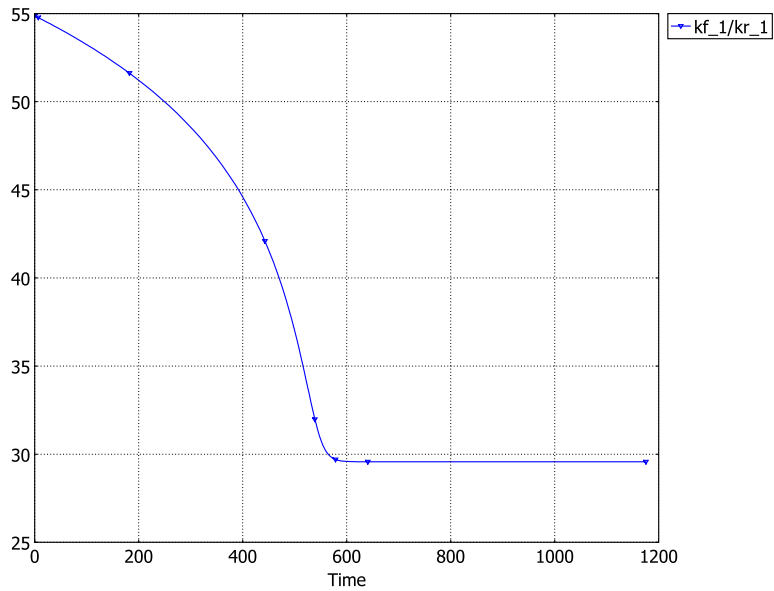
Plotting the Solution

- 1 The default plot shows the concentrations of the reactants and products as functions of time. You can see from the plot that the reaction is considerably faster in this case compared to the isothermal case discussed previously.



- 2 Click the **Plot Parameters** button on the Main toolbar.
- 3 Remove all items from the **Quantities to plot** list by clicking the << button.
Next look at the equilibrium expression during the experiment and compare it to the relationship between the concentrations in the mixture. Also compare it to the temperature deviation from the initial concentration of 700 K.
- 4 While still in the **Plot Parameters** dialog box, go to the **Expression** edit field, type k_f_1/k_r_1 , and then click the corresponding > button to plot the equilibrium expression throughout the entire experiment.

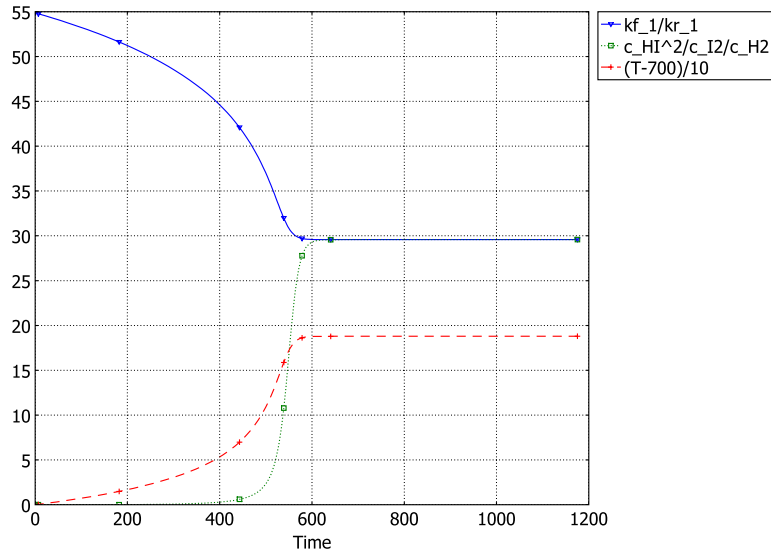
- 5 Click **OK**. The equilibrium expression varies with the temperature.



Finally, compare these results with the actual relationship between the concentrations.

- 6 Click the **Plot Parameters** button.
- 7 In the **Expression** edit field, type $c_{HI}^2/c_{I2}/c_{H2}$, then click the corresponding **>** button.
- 8 In the **Expression** edit field, type $(T - 700) / 10$, then click the corresponding **>** button.

9 Click **OK** to create this plot:



This figure shows several things:

- The system reaches steady state after approximately 600 s.
- The temperature ceases to increase at roughly 890 K.
- The relationship between the concentrations coincides with the corresponding equilibrium expression.

Space-Dependent Reacting Systems: Varying Temperature in Time

For the third case in this suite of models treating the HI reactor, introduce space dependency into the model. This means that you need to export the model from the Reaction Engineering Lab into the Chemical Engineering Module in COMSOL Multiphysics. For this scenario, the modeling procedure in the Reaction Engineering Lab is as follows:

- 1 Start COMSOL Reaction Engineering Lab.
- 2 Select the type of fluid (gas) and activate the energy balance.
- 3 Set up a new reaction and enter the expression for the HI reaction described above.
- 4 Set the initial concentrations for H_2 , I_2 , and HI.

- 5 Set the thermodynamic properties of H_2 , I_2 , and HI .
- 6 Set the transport properties of H_2 , I_2 , and HI .
- 7 Export to the Chemical Engineering Module.
- 8 Set the boundary conditions and compute the solution in COMSOL Multiphysics.

In order to perform the export step in the modeling procedure, you need some data to calculate the system's transport properties:

- The molar weight of H_2 , I_2 , and HI
- The characteristic length of the Lennard-Jones potential for H_2 , I_2 , and HI
- The energy minimum of the Lennard-Jones potential for H_2 , I_2 , and HI
- The dipole moment for H_2 , I_2 , and HI

You can find this data in Ref. 2.

The model studies the time it takes for the reacting system to reach uniform conditions in a small measuring cell. The external temperature is 710 K, while the initial system temperature is 700 K.

You can now examine the detailed instructions that reproduce the model. The procedure is identical to the previous model until the point where you set the thermodynamic properties. After that point you have to provide the transport properties and export the reaction model to the Chemical Engineering Module.

Model Library path: Education/spacedependent_hi_reactor

Model Library path: Reaction_Engineering_Lab/Education/
spacedependent_hi_reactor

MODELING IN THE REACTION ENGINEERING LAB

Defining the Reactions

- 1 Double-click the Reaction Engineering Lab icon on the desktop to open the **Model Navigator**.
- 2 Click the **New** button.
- 3 Go to the **Model** menu and select **Model Settings**.

- 4 Select the **Calculate thermodynamic properties**, the **Calculate species transport properties**, and the **Include energy balance** check boxes.
- 5 Click **Close**.
- 6 Click the **Reaction Settings** button on the Main toolbar.
- 7 Click the **New** button in the lower-left corner of the **Reactions** page.
- 8 Go to the **Formula** edit field and type $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$, then press the Enter key.
- 9 Select the **Use Arrhenius expressions** check box.
- 10 Go to the **Arrhenius parameters** area. Find the column for the **forward** reaction. In the **A** edit field for the **Frequency factor** type $8.87\text{e}7$, then in the **E** edit field for the **Activation energy** type $167\text{e}3$.
- 11 Locate the column for the **reverse** reaction. In the **A** edit field for the **Frequency factor** type $3.00\text{e}7$, then in the **E** edit field for **Activation energy** type $184\text{e}3$.

The Species Selection List

- 1 Click the **Species** tab to review the **Species selection** list and the corresponding material balances for each species. Click on species **H2**, then in the **c₀** edit field for the **Initial concentration** type 8.71 .
- 2 Click the **Thermo** tab. Enter the appropriate numbers in the first row (corresponding to H_2 in Table 2-1 in the edit fields labeled **a_{low,k}**. To use the same polynomials for the entire temperature interval, type 50 in the **lower** edit field for the **Temperature interval limits**, then type 3000 in the **midpoint** and **upper** edit fields. When you click on either of the **Polynomial coefficients** edit fields a table appears, and its rows are ordered identical to the input data listed in Table 2-1: $a_1, a_2, a_3, a_4, a_5, h_{0,0K}/R_g$, and $s_{0,0K}/R_g$.
- 3 Click the **General** tab.
- 4 In the **Species selection** list click **I2**, then in the **c₀** edit field for the initial concentration type 8.71 .
- 5 Click the **Thermo** tab and set the **Temperature interval limits**: type 50 in the **lower** edit field, 3000 in the **midpoint** edit field, and 3000 in the **upper** edit field.
- 6 Enter values in the **a_{low,k} Polynomial coefficients** edit fields, which correspond to I_2 in Table 2-1.
- 7 Click the **General** tab.
- 8 In the **Species selection** list click **HI**, then in the **c₀** edit field, make sure that the initial concentration is set to 0 (the default value).

- 9 Click the **Thermo** tab and specify the **Temperature interval limits**: type 50 in the **lower** edit field, 3000 in the **midpoint** edit field, and 3000 in the **upper** edit field.
- 10 Enter values in the lower **Polynomial coefficient**, $a_{low,k}$ edit field corresponding to HI in Table 2-1.
- 11 In the **Species selection** list, click **H2**.
- 12 In the **General** tab, type $2e-3$ in the **Molecular weight** edit field.
- 13 Click the **Transport** tab and type 2.827 in the **Potential characteristic length** edit field, type 59.7 in the **Potential Energy minimum** edit field, and make sure that the value is 0 in the **Dipole moment** edit field (the default value).
- 14 In the **Species selection** list, click **I2**.
- 15 Click the **General** tab and type $254e-3$ in the **Molecular weight** edit field.
- 16 Click the **Transport** tab and type 5.16 in the **Potential characteristic length** edit field, 474.2 in the **Potential energy minimum** edit field, and 1.3 in the **Dipole moment** edit field.
- 17 In the **Species selection** list, click **HI**.
- 18 Click the **General** tab and type $127e-3$ in the **Molecular weight** edit field.
- 19 Click the **Transport** tab and type 4.211 in the **Potential characteristic length** edit field, 288.7 in the **Potential energy minimum** edit field, and 0.5 in the **Dipole moment** edit field. Click **Close**.

Exporting the Model to COMSOL Multiphysics

- 1 Choose **File>Export>Model to COMSOL Multiphysics**.
- 2 Select **1D** in the **Space dimension** list in the **Start COMSOL Multiphysics** dialog box. If COMSOL Multiphysics is already open, this dialog box does not appear; instead create a 1D geometry before starting the export from the Reaction Engineering Lab.
- 3 Click **OK**.
- 4 Go to the **Export mass balance** area. In the **Application mode** list select **Maxwell-Stefan Diffusion and Convection: New**.
- 5 Type mass in the **Group name** edit field.
- 6 In the **Export energy balance** area, select **Heat Transfer by Conduction: New** in the **Application mode** list.
- 7 Type energy in the **Group name** edit field.

8 The **Export to COMSOL Multiphysics** dialog box should now look like this:

Export to COMSOL Multiphysics

Geometry: Geom1 (1D)

Domain level: Subdomain

Export mass balance

Settings Species Mapping Variables

Application mode: Maxwell-Stefan Diffusion and Convection: New

Application mode name: chms

Group name: mass

☒ Export energy balance

Settings Variables

Application mode: Heat Transfer by Conduction: New

Dependent variable: T

Application mode name: ht

Group name: energy

☐ Export momentum balance

Settings Variables

Application mode:

Dependent variables:

Application mode name:

Group name:

Export Cancel Apply Help

9 Click **Export**.

Modeling in COMSOL Multiphysics

1 Choose **Draw>Specify Objects>Line**.

2 Enter 0.5×10^{-3} in the **x** edit field, and click **OK**.

3 Click the **Zoom Extents** toolbar button (or choose **Options>Zoom>Zoom Extents**).

4 Choose **Multiphysics>Maxwell-Stefan Diffusion and Convection (chms)**.

5 Choose **Physics>Subdomain Settings**.

6 Select subdomain 1 from the **Subdomain selection** list.

7 Select **mass** from the **Group** list below the list on the **Subdomains** tab.

8 Click **OK**.

You have now applied the settings exported from Reaction Engineering Lab for the mass balance.

9 Choose **Physics>Boundary Settings**.

10 In the **Boundaries** list, select **1** and **2**. Verify that the default boundary condition, **Insulation/symmetry**, is selected for both **w_H2** and **w_I2**. Click **OK**.

Note that you do not need to set any conditions for **w_HI**; it depends on the fluxes of the two other species. COMSOL Multiphysics obtains the flux of **w_HI** from the flow velocity (0 in this case) and the fact that the sum of all mass fluxes should give the total mass flux (0 in this case because the flow velocity is 0).

11 Choose **Multiphysics>Heat Transfer by Conduction (ht)**.

12 Choose **Physics>Subdomain Settings**.

13 Select **energy** in the **Group** list below the list in the **Subdomains** tab.

14 Click **OK**.

This applies the exported settings from Reaction Engineering Lab to describe the energy balance equation.

15 Choose **Physics>Boundary Settings**.

16 In the **Boundaries** list select **2**, and in the **Boundary condition** list select **Temperature**.

17 Type 710 in the **Temperature** edit field.

18 Click **OK**.

19 Click the **Refine Mesh** button on the Main toolbar twice (or choose **Mesh>Refine Mesh** twice).

20 Click the **Solve** button on the Main toolbar (or choose **Solve>Solve Problem**). This solves the model.

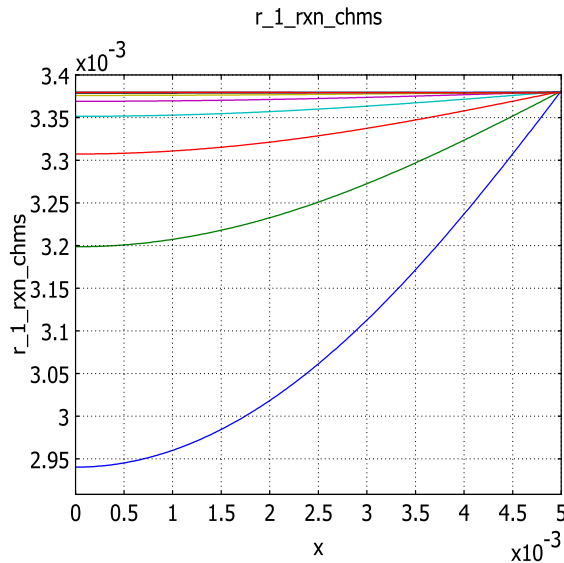
To study how the reaction rate varies in space and time, set up a new plot as follows:

1 Choose **Postprocessing>Domain Plot Parameters**.

2 Click the **Line/Extrusion** tab and type **r_1_rxn_chms** in the **Expression** edit field. This corresponds to the reaction rate as defined in the Reaction Engineering Lab.

3 Click the **General** tab and select all time steps from **0.1** to **1** s from the **Solutions to use** list (first select **0.1**, then press Shift and select the last time to get the whole selection).

4 Click **OK**.



The plot shows that the reaction distribution in the reactor quickly becomes uniform, due to the small size of the reactor and the fast transport in the gas phase at 700 K.

Model Validation and Calibration

The following section gives an overview of the Parameter Estimation functionality of the Reaction Engineering Lab, allowing you to validate and calibrate your model to experimental data. A number of basic examples are outlined, treating typical applications of parameter estimation:

- Finding rate constants for isothermal systems.
- Evaluating Arrhenius parameters for non-isothermal systems.
- Determining reaction order.
- Estimating non-kinetic parameters.

Working with parameter estimation problems typically involves the following steps:

- Formulating a reaction model by entering the chemical reactions and selecting a reactor type.
- Reading experimental data into the graphical user interface.
- Associating measured variables with the variables of the reaction model.

- Selecting parameters and performing estimation by minimizing the objective least-squares function.
- Evaluating the ability of the model to represent the experimental data.

Apart from the examples below you can also find a number of more advanced models in the model library.

DETERMINING RATE CONSTANTS

Determining rate constants for chemical reactions occurring at constant temperature is perhaps the most common application of parameter estimation in chemistry and chemical engineering.

Consider the irreversible reaction:



If the chemistry occurs in a closed and perfectly mixed system, then the mathematical model is given by:

$$\frac{dc_A}{dt} = -kc_A \quad (2-2)$$

$$\frac{dc_B}{dt} = kc_A \quad (2-3)$$

The model described by Equation 2-2 and Equation 2-3 is automatically set up in the Reaction Engineering Lab as you select the Batch reactor type and enter the reaction formula into the graphical user interface.

The image shows a 'Reaction Settings' dialog box with two tabs: 'Reactions' and 'Species'. The 'Reactions' tab is active, showing a list of reactions under 'Reaction selection'. The first reaction, '1: A=>B', is selected. Below the list are buttons for 'New', 'Delete', and 'Reset'. To the right, the 'Formula' field contains 'A=>B' and the 'Type' is set to 'Irreversible'. Below this, the 'Kinetics' tab is selected, showing options for 'Use Arrhenius expressions' and 'Arrhenius parameters'. The 'Arrhenius parameters' section includes a table for forward and reverse reaction parameters (A, n, E) with units and descriptions. Below this, the 'Kinetic expressions' section includes a table for forward rate constant (k^f), reverse rate constant (k^r), equilibrium constant (K^{eq}), and reaction rate (r), with units and descriptions. The 'Specify equilibrium constant' checkbox is unchecked.

Quantity	Value/Expression	Unit	Description
A	1		Frequency factor
n	0		Temperature exponent
E	0	J/mol	Activation energy

Quantity	Value/Expression	Unit	Description
k^f	1		Forward rate constant
k^r	0		Reverse rate constant
K^{eq}	0		Equilibrium constant
K^{eq}	0		Equilibrium expression
r	$k^f_1 * c_A$	mol/(m ³ s)	Reaction rate

Figure 2-2: You define the kinetics of the reaction model by typing in reaction formulas in the Reaction Settings dialog box.

In order to estimate the reaction rate constant (k) the mathematical model has to be correlated with experimental data. Start by loading the experimental data into the software and then continue with the parameter estimation procedure within the

Reaction Engineering Lab GUI. In the present example you import data points describing the concentration of species A as a function of time.

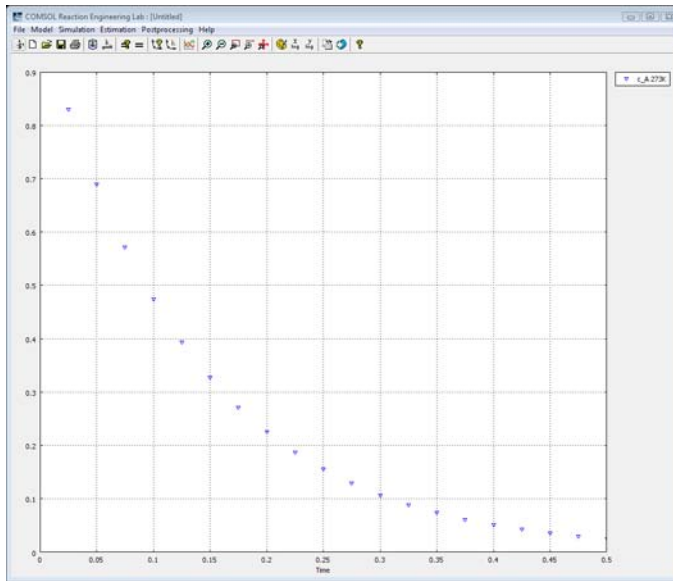


Figure 2-3: Import the experimental data directly into the graphical user interface.

The next step requires association of the measured variables with the variables of the reaction model. In this case, the measured variable is the concentration of species A, corresponding to a state variable of the model, c_A . Once the parameters you want to

estimate have been specified, the software is set up to solve the parameter estimation problem.

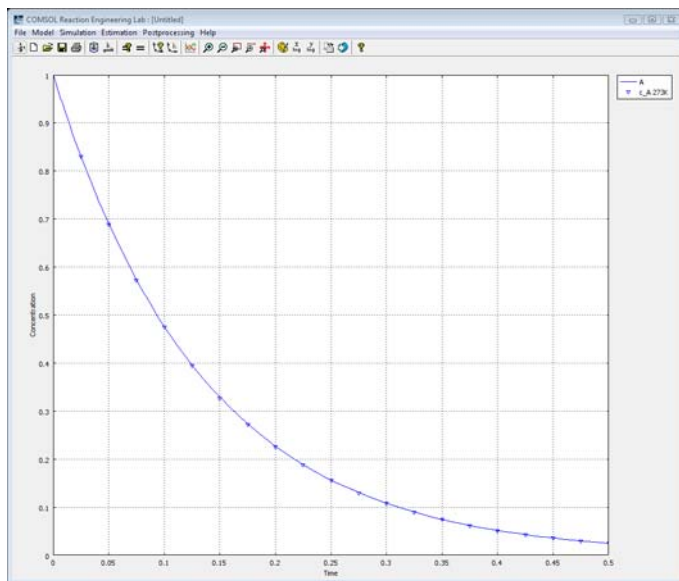


Figure 2-4: Once the rate constant has been estimated the simulated and experimental results can be plotted simultaneously.

The following steps show you how to set up and solve the parameter estimation problem outlined above.

Model Library path: Education/parameter_estimation_isothermal

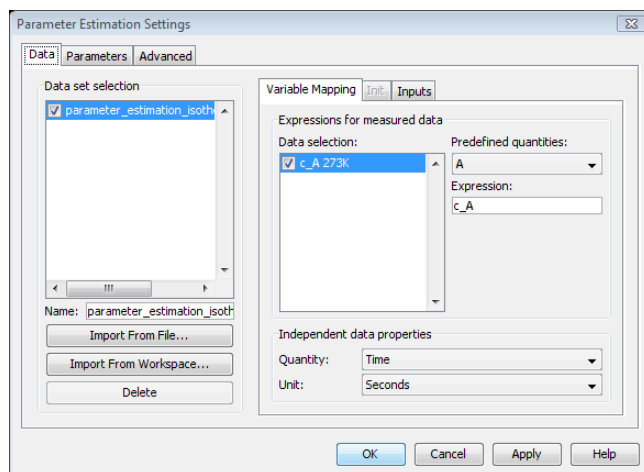
- 1 Start the Reaction Engineering Lab. In the **Model Navigator**, click the **New** button.
- 2 Select the menu item **Model>Reaction Settings**.
- 3 On the **Reactions** page, create a new entry in the **Reaction selection** list by clicking the **New** button.
- 4 Type $A \Rightarrow B$ in the **Formula** edit field.
- 5 Click the **Species** tab.
- 6 Select A from the **Species selection** list and type 1 in the **c_0** edit field.
- 7 Click **Close**.

This concludes the definition of the reaction model where the mass balance equations, Equation 2-2 and Equation 2-3, describing an isothermal batch reactor system are set up. Note that the isothermal batch reactor is the default reactor system in Reaction Engineering Lab. Employing other reactor types requires that the appropriate selections are made in the **Model Settings** dialog box.

Now, move on to import the experimental results and associate the variables of the measured data with the variables of the reaction model:

- 1 Select the menu item **Estimation>Parameter Estimation Settings**.
- 2 Click the **Import From File** button, browse to the text file `parameter_estimation_isothermal_data.txt`. Select the file and click **Import**.
- 3 As the name of the text file appears in the **Data set selection** list, select it.
- 4 On the **Variable Mapping** page, note that the measured variable name, `c_A 273K`, is mapped to the model variable `c_A`, by default.

The independent variable of the measured data is assumed to be represented in the first column in the imported data file. In the present example the data has been collected at a number of different times (seconds). This corresponds to the default selections in the **Independent data properties** area, set to **Time (Seconds)**.



In the next step, select the parameters you want to estimate.

- 1 In the **Parameter Estimation Settings** dialog box, go to the **Parameters** page.

- 2 Select **kf_1 (Forward rate constant 1)** from the **Predefined parameters** list and click **Add (>)**.

Note that the initial guess of the parameter is taken from the value specified in the reaction model. In this case the value of the parameter **kf_1** is found in the **Forward rate constant** edit field, in the **Reaction Settings** dialog box. The default value is 1.

- 3 Click **OK** to close the **Parameter Estimation Settings** dialog box.

Finally, solve the parameter estimation problem.

- 1 Click the **Estimate Parameters** button on the Main toolbar.

You find the estimated value of the rate constant **kf_1** and its confidence limits displayed in the **Log - Progress** window. If the **Log - Progress** window is not open, access it by following the steps below:

- 1 Select the menu item **Estimation>View Log**.

- 2 Click the **Log** page.

Note that you may have to scroll in the log to locate the summary report of the parameter estimation calculations. Selecting the **Close automatically** check box closes the **Log - Progress** window after each simulation.

You can have the software automatically update the reaction model with the new parameter value. In this example, you then find the updated value (7.411) in the **Forward rate constant** edit field, in the **Reaction Settings** dialog box. It is also your option to have the software automatically run the model simulation with the updated parameters. To set these options, follow these steps.

- 1 Select the menu item **Estimation>Parameter Estimation Settings**.
- 2 Go to the **Advanced** page.
- 3 Make sure that the check box **Copy parameter values to model after parameter estimation** is selected.
- 4 Make sure that the check box **Solve model after estimating parameters** is selected.
- 5 Click **OK**.

DETERMINING ARRHENIUS PARAMETERS

In the previous example you evaluated the rate constant, k , under isothermal conditions. Under non-isothermal conditions, Reaction Engineering Lab allows you to express the rate constants according to the Arrhenius law:

$$k = A \exp\left(\frac{-E}{R_g T}\right) \quad (2-4)$$

In Equation 2-4, A represents the frequency factor, E the activation energy (J/mol), R_g the ideal gas constant (J/(mol·K)), and T the temperature (K). Making use of a series of estimates for k , evaluated from experiments run at different temperatures, the software can calculate the Arrhenius parameters A and E .

The way to set up and solve this type of estimation problem is very similar to the isothermal case. The difference is that the software takes multiple data sets as input for the calculations. In the present example, concentration transients of species A are available at three different temperatures; 400 K, 500 K, and 600 K.

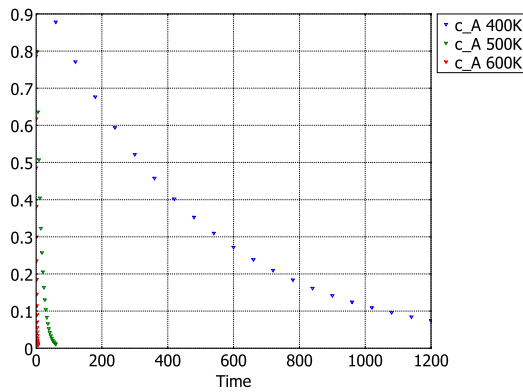


Figure 2-5: Three data sets are read into the software, representing concentration transients of species A at 400 K, 500 K, and 600 K.

When working with multiple data sets, each set is associated with a parameter that is known exactly, in this case the temperature. The known temperature affects the reaction model and is specified when setting up the parameter estimation problem.

When the software calculates the Arrhenius parameters, all experimental data sets are taken into account simultaneously.

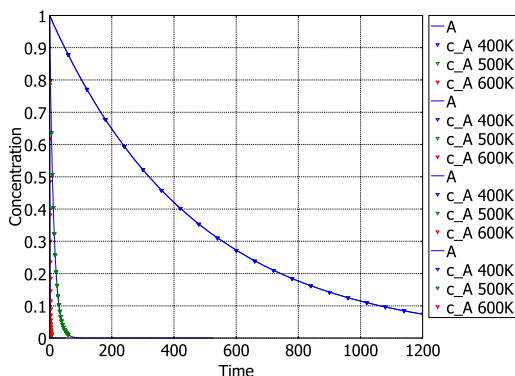


Figure 2-6: When the Arrhenius parameters have been estimated, the simulated and experimental results are plotted in the same graph.

The following steps illustrate how to evaluate the Arrhenius parameters appearing in Equation 2-4.

Model Library path: Education/parameter_estimation_nonisothermal

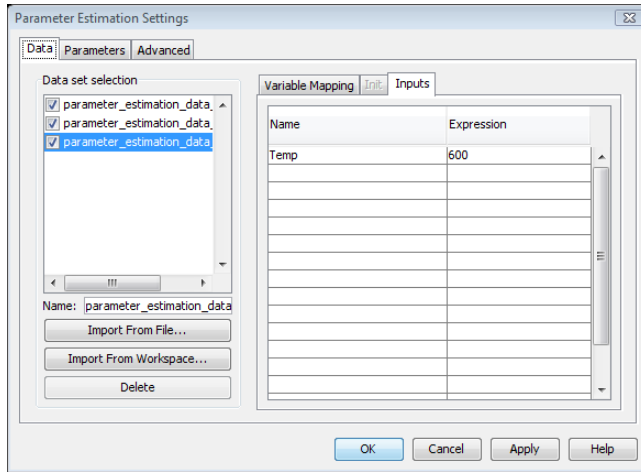
- 1 Start the Reaction Engineering Lab. In the **Model Navigator**, click the **New** button.
- 2 Select the menu item **Model>Model Settings**.
- 3 Type Temp in the **Temperature** edit field.
This is the parameter name you will use when accounting for the fact that data sets refer to experiments performed at different temperatures.
- 4 Click **Close**.
- 5 Select the menu item **Model>Constants**.
- 6 Type Temp in the **Name** column and 400 in the **Expression** column.
- 7 Click **OK**.
- 8 Select the menu item **Model>Reaction Settings**.
- 9 On the **Reactions** page, create a new entry in the **Reaction selection** list by clicking the **New** button.

- 10 Type $A \Rightarrow B$ in the **Formula** edit field.
- 11 Click the **Use Arrhenius expressions** check box.
- 12 Click the **Species** tab.
- 13 Select A from the **Species selection** list and type 1 in the **c₀** edit field.
- 14 Click **Close**.

Now, move on to import experimental data sampled at 400 K, 500 K, and 600 K.

- 1 Select the menu item **Estimation>Parameter Estimation Settings**.
- 2 Go to the **Data** page.
- 3 Click the **Import From File** button, browse to the text file `parameter_estimation_data_400K.txt`. Select the file and click **Import**.
- 4 In the same way, import the files `parameter_estimation_data_500K.txt` and `parameter_estimation_data_600K.txt`.
- 5 Select the `parameter_estimation_data_400K.txt` entry from the **Data set selection** list.
- 6 Click the **Inputs** page.
- 7 Type Temp in the **Name** column and 400 in the **Expression** column.
- 8 Repeat the process according to the table below:

DATA SET	TEMP
<code>parameter_estimation_data_500K.txt</code>	500
<code>parameter_estimation_data_600K.txtt</code>	600

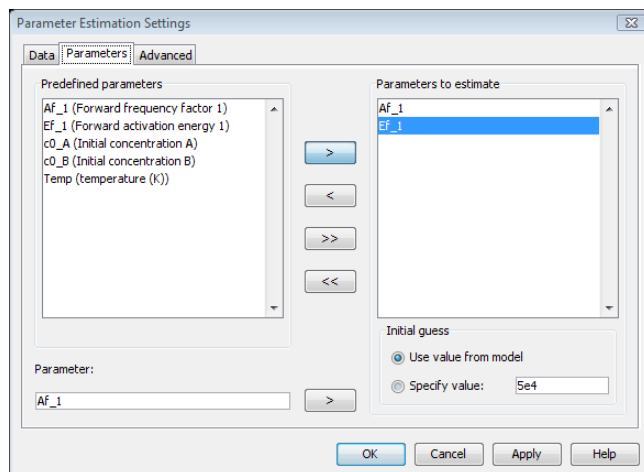


In the next step, select the parameters you want to estimate.

- 1 In the **Parameter Estimation Settings** dialog box, go to the **Parameters** page.
- 2 Select **Af_I (Forward frequency factor I)** and **Ef_I (Forward activation energy I)** from the **Predefined parameters** list and click **Add (>)**.

- 3 Provide initial guesses for the parameters by selecting the appropriate entry in the **Parameters to estimate** list and typing the value into the **Specify value** edit field:

PARAMETER	INITIAL GUESS
Af_1	1e5
Ef_1	5e4



Here you specify the parameters initial values in the **Parameter Estimation Settings** dialog box. You can of course also choose the current values provided in the reaction model. To provide initial guesses within the model, go to the **Reaction Settings** dialog box and type the values in the **Frequency factor** and **Activation energy** edit fields.

- 4 Click **OK** to close the **Parameter Estimation Settings** dialog box.

Finally, solve the parameter estimation problem:

- 1 Click the **Estimate Parameters** button on the Main toolbar.

By default the calculated parameters are updated to the reaction model. In the present model you find the values of Af_1 and Ef_1 in the **Frequency factor** and **Activation energy** edit fields, as you open the **Reaction Settings** dialog.

You can also find the estimated values of Af_1 and Ef_1 and the associated confidence limits in the **Log - Progress** window. If the **Log - Progress** window is not open, access it using the following steps:

- 2 Select the menu item **Estimation>View Log**.

3 Click the **Log** page.

Note that you may have to scroll in the log to locate the summary report of the parameter estimation calculations. Selecting the **Close automatically** check box closes the **Log - Progress** window after each simulation.

DETERMINING REACTION ORDER

The path of a chemical reaction can consist of a large number of steps with intermediate species that do not appear in the net reaction. In many cases, you want to estimate the influence of the reactant and product concentrations on the reaction rate without modeling the intermediate concentrations. Within a certain range of composition, such an approximation can be satisfactory for setting up materials and energy balances of a system. These types of simplified kinetic models therefore require that you fit the reaction order of the reactant and product concentrations in the net reaction to experimental measurements of concentration as a function of time.

Suppose that molecularity of the overall reaction is unknown:



If the chemistry occurs in a perfectly mixed system, then the mathematical model is given by:

$$\frac{dc_A}{dt} = -kc_A^n \quad (2-6)$$

$$\frac{dc_B}{dt} = kc_A^n \quad (2-7)$$

In this case, you can have the software estimate both the rate constant (k) and the reaction (n) order simultaneously. In more complicated reaction networks, where multiple reaction orders and rate constants are to be evaluated, it is often a good approach to start by setting reaction orders as constant integers and then evaluate the rate constants. Investigating the model fit to data for a number of different reaction order combinations then allows you to choose the appropriate model. Such an approach is exemplified in the model Kinetic Modeling of Cinnamaldehyde Hydrogenation, found in the Model Library.

Follow the steps below to estimate the reaction order n and rate constant k for the system just described.

Model Library path: Education/parameter_estimation_rxnorder

- 1 Start the Reaction Engineering Lab. In the **Model Navigator**, click the **New** button.
If you already have Reaction Engineering Lab open, select the menu item **File>New**.
- 2 Select the menu item **Model>Reaction Settings**.
- 3 On the **Reactions** page, create a new entry in the **Reaction selection** list by clicking the **New** button.
- 4 Type $A \Rightarrow B$ in the **Formula** edit field.
- 5 Modify the automatically generated reaction rate expression by typing $k_f_1 * c_A^n$ in the **r** edit field.
- 6 Click the **Species** tab.
- 7 Select A from the **Species selection list** and type 1 in the **c₀** edit field.
- 8 Click **Close**.
- 9 Choose **Model>Constants**.
- 10 Type n in the **Name** column and 1 in the **Expression** column.
- 11 Click **OK**.

This concludes the definition of the reaction model where the mass balance equations, Equation 2-6 and Equation 2-7. Note that you modified the reaction rate expression by raising the concentration c_A to the power n. The user-defined parameter n corresponds to the reaction order and was defined in the **Constants** dialog, with an initial guess $n = 1$.

Now, move on import the experimental data and associate the variables of the experimental data with the variables of the reaction model:

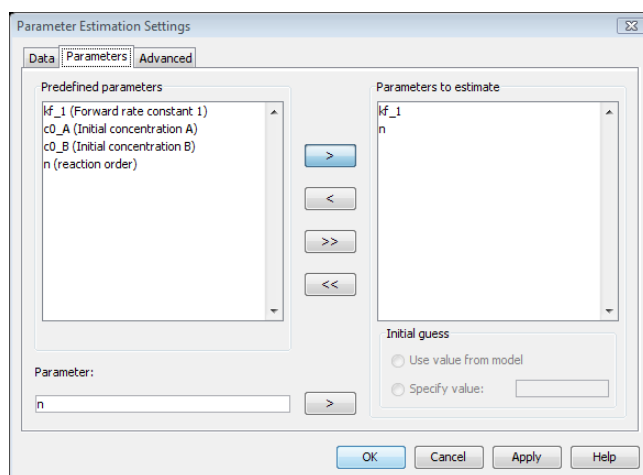
- 1 Select the menu item **Estimation>Parameter Estimation Settings**.
- 2 Click the **Import From File** button, browse to the text file `parameter_estimation_rxnorder_data.txt`. Select the file and click **Import**.
- 3 As the name of the text file appears in the **Data set selection** list, select it.

- 4 On the **Variable Mapping** page, note that the measured variable name, c_A data, is mapped to the model variable c_A, by default.

Note that the independent variable of the measure data is time (seconds). This corresponds to the default selections in the **Independent data properties** area, set to **Time (Seconds)**.

In the next step, select the parameters you want to estimate:

- 1 In the **Parameter Estimation Settings** dialog box, go to the **Parameters** page.
- 2 Select **kf_1 (Forward rate constant 1)** from the **Predefined parameters** list and click **Add (>)**.
- 3 Select **n** from the **Predefined parameters** list and click **Add (>)**.



Note that the initial guess of the parameter value is taken from the value specified in the reaction model. The value of the parameter kf_1 is found in the **Forward rate constant** edit field, in the **Reaction Settings** dialog box. The value of the reaction order was set in the **Constants** dialog.

- 4 Click **OK** to close the **Parameter Estimation Settings** dialog box.

Finally, solve the parameter estimation problem.

- 1 Click the **Estimate Parameters** button on the Main toolbar.

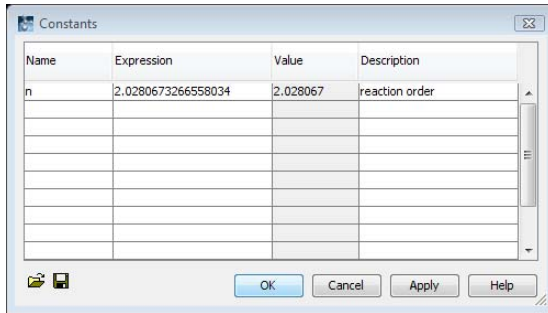
You find the estimated value of the rate constant kf_1, the reaction order n, and their confidence limits displayed in the **Log - Progress** window.

If the **Log - Progress** window is not open, access it by following the steps below:

1 Select the menu item **Estimation>View Log**.

2 Click the **Log** page.

You can have the software automatically update the reaction model with the new parameter values. You find the proper selections on the **Advanced** page in the **Parameter Estimation Settings** dialog box. In this example, you find the updated value of k_f_1 in the **Forward rate constant** edit field, and the estimated value of n in the **Constants** dialog box.



DETERMINING NON-KINETIC PARAMETERS

Nearly any parameter of a model set up in Reaction Engineering Lab can be calibrated with respect to experimental data, no matter what combination of kinetics and reactor type that you choose to simulate.

Consider the dissolution of CO in liquid, vigorously stirred in a closed vessel. The liquid phase concentration of CO can be described by the following equation:

$$\frac{dc_{CO}}{dt} = k_g(c_{sat} - c_{CO}) \quad (2-8)$$

where k_g is the mass transfer coefficient and c_{sat} is the saturation concentration of CO in the liquid. Although the saturation concentration is a function of the gas pressure and the nature of the solvent, c_{sat} will be evaluated directly from experimental data together with k_g .

The reaction model is set up by selecting the Batch reactor type, defining mass a balance by creating a new species, and typing the right-hand side of Equation 2-6 into the **R** edit field.

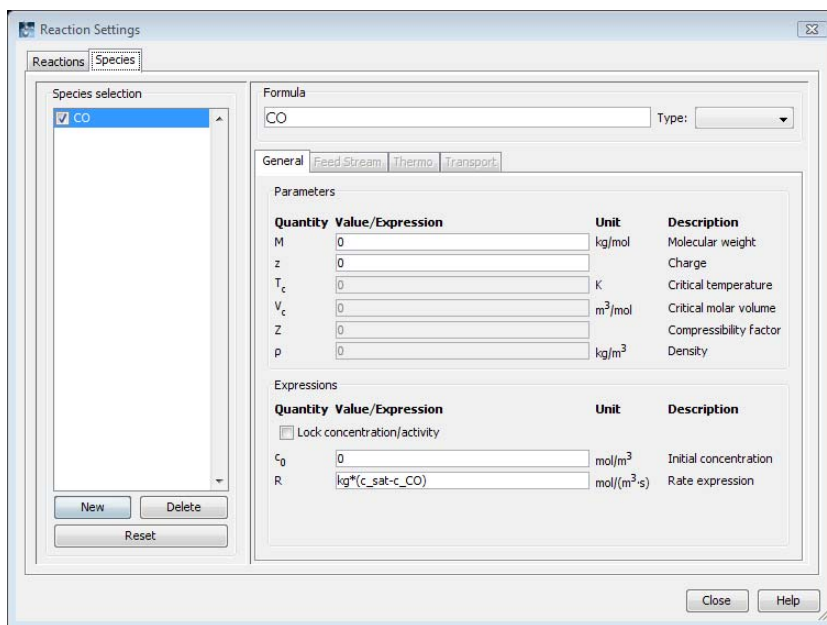


Figure 2-7: The reaction model is defined in the Reaction Settings dialog box.

You then set up and solve the parameter estimation problem by associating the experimental variables with the model variables, and selecting the parameters to estimate. Follow the steps below to estimate the mass transfer coefficient k_g and saturation concentration c_{sat} .

Model Library path: Education/parameter_estimation_CO_absorption

- 1 Start the Reaction Engineering Lab. In the **Model Navigator**, click the **New** button.
If you already have Reaction Engineering Lab open, select the menu item **File>New**.
- 2 Select the menu item **Model>Reaction Settings**.
- 3 On the **Species** page, create a new entry in the **Species selection** list by clicking the **New** button.
- 4 Type CO in the **Formula** edit field.
- 5 Type $kg*(c_{sat}-c_{CO})$ in the **Rate expression** edit field.

6 Select the menu item **Model>Constants**.

7 Type in the following entries in the **Name** column and **Expression** columns:

NAME	EXPRESSION
kg	0.1
c_sat	1

8 Click **OK**.

This concludes the definition of the reaction model where the mass balance Equation 2-8. The user-defined parameters kg and c_sat were defined in the **Constants** dialog, with the initial guesses kg = 0.1, and c_sat = 1.

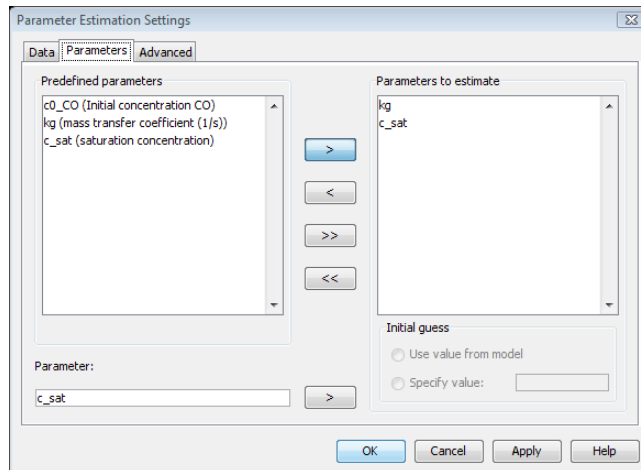
Next import the experimental data and select the parameters you want to estimate.

1 Select the menu item **Estimation>Parameter Estimation Settings**.

2 Click the **Import From File** button, browse to the text file parameter_estimation_CO_absorption_data.txt. Select the file and click **Import**.

3 Go to the **Parameters** page.

4 Select **kg** and **c_sat** from the **Predefined parameters** list and click **Add (>)**.

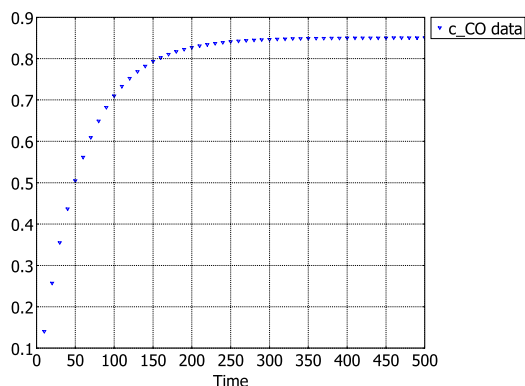


Note that the initial guess of the parameter value is taken from the value specified in the reaction model. The value of kg and c_sat were specified in the **Constants** dialog.

5 Click **OK** to close the **Parameter Estimation Settings** dialog box.

Finally, solve the parameter estimation problem.

Click the **Estimate Parameters** button on the Main toolbar.



By default the software automatically updates the reaction model with the calculated parameter values. In this example, the estimated values are retuned to the **Constants** window, updating the reaction model.

Name	Expression	Value	Description
kg	0.01791686688381621	0.017917	mass transfer coefficient (...)
c_sat	0.8506691804052687	0.850669	saturation concentration

You can also find the estimated value of kg and c_{sat} , as well as their confidence limits displayed in the **Log - Progress** window. If the **Log - Progress** window is not open, access it by following the steps below:

- 1 Select the menu item **Estimation>View Log**.
- 2 Click the **Log** page.

References

1. J.H. Sullivan, *J. Chem. Phys.*, vol. 46, p. 73, 1967.

2. B.E. Poling, J.M. Prausnitz, and J.P. O'Connell, *The Properties of Gases and Liquids*, 5th edition, McGraw-Hill, 2001.

The Modeling Environment

Introduction

To launch the Reaction Engineering Lab's graphical user interface (GUI), click the Reaction Engineering Lab desktop icon.

The GUI contains seven central components, listed here in the order you encounter them during normal work flow:

- The **Model Settings** dialog box
- The **Constants** and **Expressions** dialog boxes
- The **Reaction Settings** dialog box
- The **Solver Parameters** dialog box
- The **Parameter Estimation Parameters** dialog box
- The **Plot Parameters** dialog box
- Export to the COMSOL Script workspace and to COMSOL Multiphysics.

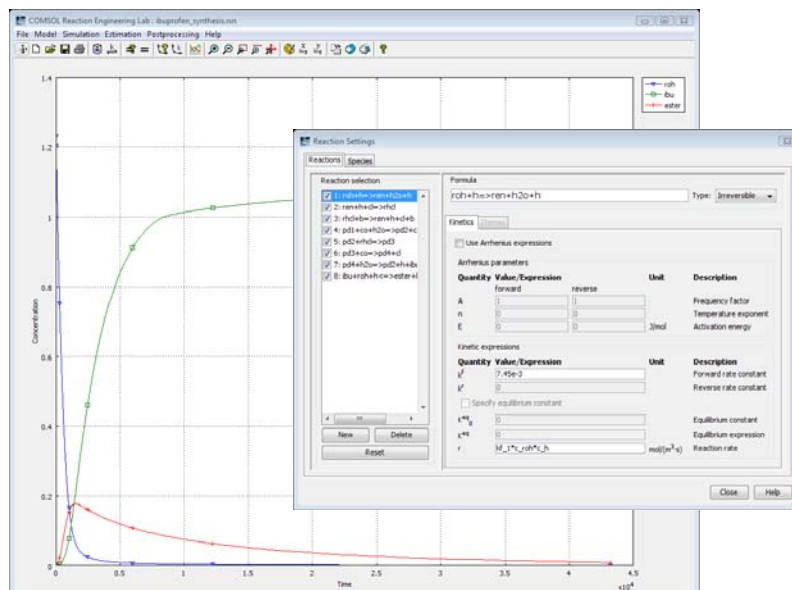


Figure 3-1: The Reaction Engineering Lab GUI and the Reaction Settings dialog box.

Models you create in the Reaction Engineering Lab are referred to as reaction models and are stored in files with the .rxn extension. A reaction model contains information

about the reaction kinetics and thermodynamics of the chemical system under study. It also contains details regarding the reacting fluid such as the fluid phase and the mixture transport properties. Furthermore, if you have run any simulations, it also stores the results.

The following paragraphs give an overview of the user-interface components; a detailed description of all user-interface features follows in later sections.

To access the **Model Settings** dialog box, select **Model>Model Settings** on the menu bar or click the corresponding quick button on the Main toolbar. Options in this dialog box determine which balance equations (material and energy) and transport properties that are included in the model and also the phase of the fluid (gas or liquid) in which the chemistry takes place. Specifying these system characteristics constitutes the natural starting point when creating a reaction model.

You access the **Reaction Settings** dialog box by selecting **Model>Reaction Settings** on the menu bar or by clicking the corresponding quick button on the Main toolbar. This dialog box presents two main interfaces:

- In the Reactions interface you set up the kinetics of the chemical reaction networks. When you type in the chemical-reaction formulas, the Reaction Engineering Lab automatically generates the corresponding reaction rate expressions. Apart from reversible and irreversible reactions, the Reaction Engineering Lab also handles reactions at chemical equilibrium. For a given reaction you specify rate constants or equilibrium constants.
- The Species interface deals with information concerning the reactants, intermediates, and products participating in a given chemistry. The information you enter and that the Reaction Engineering Lab generates in the Species interface forms natural building blocks for expressing composite properties related to chemical reactions and fluid transport. For instance, the Reaction Engineering Lab uses species-specific thermodynamic properties to calculate a reaction's thermodynamic properties; transport properties of a fluid mixture depend on the properties of its pure components. The main functionality of the Species interface is to organize and describe thermodynamic and transport data in this regard. The Reaction Engineering Lab uses predefined expression in order to calculate transport properties for gases at moderate pressure and for a limited set of liquids, for example, aqueous solutions.

From the **Parameter Estimation Settings** dialog box you set up parameter estimation problems. Access this window by selecting the menu item **Estimation>Parameter Estimation Settings**. Using the dialog box you typically import experimental data into

the software and associate the measured variables with the variables of your reaction model. When you click the **Estimate Parameters** button, Reaction Engineering Lab will start searching for values of selected model parameters that calibrate your theoretical model to the experimental data.

Access the **Solver Parameters** dialog box by selecting **Simulation>Solver Parameters** or by selecting the corresponding icon from the Main toolbar. In this dialog box you enter the simulation's time scale as well as solver specifications.

To configure plot parameters you likewise work with a dialog box accessible either by making a selection from the **Postprocessing** menu or by clicking the corresponding quick button on the Main toolbar. Here you decide which model results to display and how they appear. You can plot any solution variable, predefined expression, or user-defined expression in either the main user interface or in separate plot windows.

The Reaction Engineering Lab is fully integrated in the COMSOL product family. For further analysis in other COMSOL software products, you can link reaction models from the Reaction Engineering Lab environment. Export model data to the COMSOL Script workspace to run reaction models from the command line, perform parametric studies and advanced postprocessing. Use the **Export to COMSOL Multiphysics** to transfer the chemistry and physics of reactions models to COMSOL Multiphysics, extending your analysis to time and space-dependent models. Reaction Engineering Lab can export to application modes of the Chemical Engineering Module, the MEMS Module, as well as the Earth Science Module.

The Model Navigator

When starting the Reaction Engineering Lab, you are greeted by the **Model Navigator**.

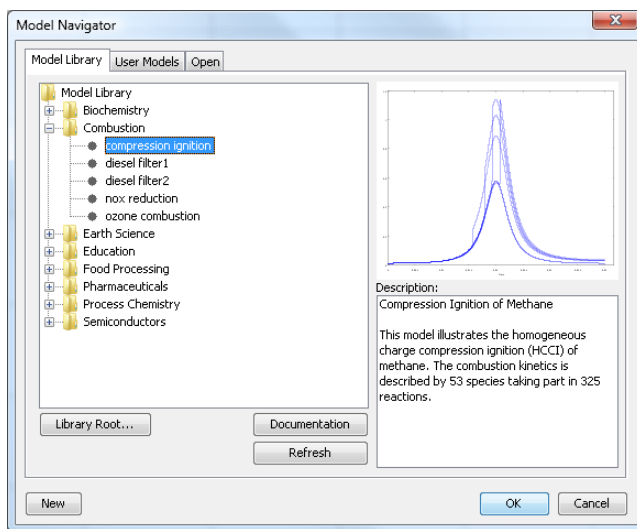


Figure 3-2: The Reaction Engineering Lab Model Navigator.

The Model Navigator allows you to browse and select from reaction models and also to view associated documentation. You find a collection of solved reaction models on the **Model Library** page, where different folders group the models into different application areas. You can load the models for inspection or modification, either in the Reaction Engineering Lab (Model RXN-file) or in COMSOL Multiphysics (Model MPH-file, which requires COMSOL Multiphysics). Selecting a model in the list to the left produces a model image and a short model summary in the **Description** area to the right. To access documentation about the model, click the **Documentation** button.

Clicking the **Library Root** button allows you to specify the path to your model directories in order to access models from the **User Models** tab in later modeling sessions.

To browse for and open a model, click the **Open** tab and use the **Look in** list to find the file that you want to open. Click **OK** to open the file.

To build a new model from scratch, click the **New** button in the **Model Navigator**.

Select **File>Reaction Model Properties** to open the dialog box in Figure 3-3. Here you can enter basic information about a model, information that you can display in the **Model Navigator** when single-clicking a model name on the **User Models** tab. Select **File>Save Model Image** to associate an image to the model description. The **Model Navigator** displays both the model image and the model description.

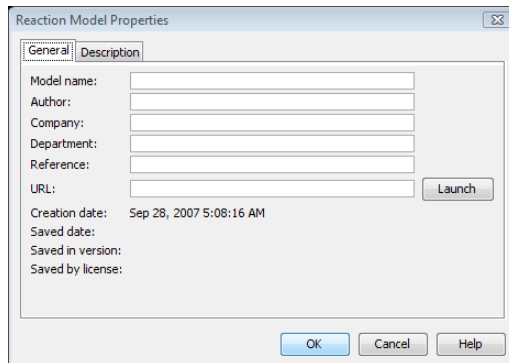


Figure 3-3: The Reaction Model Properties dialog box.

Model Settings

The **Model Settings** dialog box (Figure 3-4) is the natural starting point when building a new model. You can access it by selecting **Model>Model Settings** or by clicking the corresponding quick button on the Main toolbar.

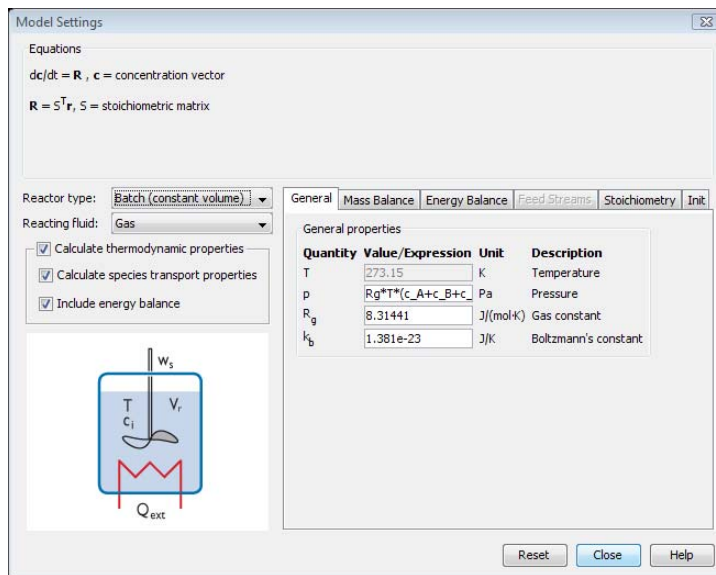


Figure 3-4: The Model Settings dialog box.

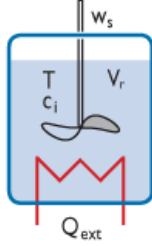
In the **Reactor type** list you can choose from a set of predefined chemical reactors:

- Batch reactor
- Batch reactor with constant volume
- Semibatch reactor
- Continuous stirred tank reactor (CSTR) with constant volume
- Continuous stirred tank reactor (CSTR) with constant mass
- Plug-flow reactor

The default reactor selection in the Reaction Engineering Lab is the **Batch (constant volume)** reactor, running under isothermal conditions. Common for all reactor models is that reacting fluids in the gas phase are assumed to behave as ideal gases. Liquid mixtures are assumed to be ideal and incompressible.

The Batch Reactor

In the batch reactor, no mass enters or leaves the system.



The species mass balances are given by:

$$\frac{d(c_i V_r)}{dt} = V_r R_i \quad (3-1)$$

which takes into account the effect of changing volume. In Equation 3-1, c_i is the species molar concentration (mol/m^3), V_r denotes the reactor volume (m^3), and R_i is the species rate expression ($\text{mol}/(\text{m}^3 \cdot \text{s})$).

For an ideal reacting gas, the energy balance is:

$$V_r \sum_i c_i C_{p,i} \frac{dT}{dt} = w_s + Q + Q_{\text{ext}} + V_r \frac{dp}{dt} \quad (3-2)$$

In Equation 3-2 $C_{p,i}$ is the species molar heat capacity ($\text{J}/(\text{mol} \cdot \text{K})$), T is the temperature (K), and p the pressure (Pa). On the right hand side, w_s represents additional work, for instance the shaft work (J/s). Q is the heat due to chemical reaction (J/s), and Q_{ext} denotes heat added to the system (J/s). The heat of reaction is:

$$Q = -V_r \sum_j H_j r_j \quad (3-3)$$

where H_j is the enthalpy of reaction ($\text{J}/(\text{mol K})$), and r_j the reaction rate ($\text{mol}/(\text{m}^3 \cdot \text{s})$).

For an incompressible and ideally mixed reacting liquid, the energy balance is:

$$V_r \sum_i c_i C_{p,i} \frac{dT}{dt} = w_s + Q + Q_{\text{ext}} \quad (3-4)$$

You find Equation 3-1 displayed in the **Equations** area of the **Model Settings** dialog box. If an energy balance is included in your model, you find Equation 3-2 or Equation 3-4 displayed in the **Equations** area when the **Energy Balance** page is selected.

The Batch Reactor with Constant Volume

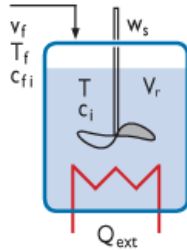
The constant volume batch reactor is the default selection in the Reaction Engineering Lab. It assumes a closed, perfectly mixed system of constant volume. The species mass balances are:

$$\frac{dc_i}{dt} = R_i \quad (3-5)$$

For an ideal reacting gas, the energy balance is given by Equation 3-2. For an incompressible and ideally mixed reacting liquid, the energy balance is given by Equation 3-4.

The Semibatch Reactor

In the semibatch reactor, reactants enter the reactor by means of one or several feed streams.



The species mass balances are given by:

$$\frac{d(c_i V_r)}{dt} = v_{f,i} c_{f,i} + R_i V_r \quad (3-6)$$

In Equation 3-6, $c_{f,i}$ is the species molar concentration (mol/m³) of the associated feed stream $v_{f,i}$ (m³/s). V_r denotes the reactor volume (m³) and is a function of time. For ideal mixtures:

$$\frac{dV_r}{dt} = \sum v_{f,i} + v_p \quad (3-7)$$

The term v_p denotes the volumetric production rate due to reaction (m³/s):

$$v_p = \sum_j \sum_i v_{ij} \frac{M_i}{\rho_i} r_j V_r \quad (3-8)$$

where v_{ij} is the stoichiometric coefficient of species i in reaction j , M_i denotes the species molecular weight (kg/mol), ρ_i the species density (kg/m³), and r_j is the reaction rate (mol/(m³·s)) of reaction j .

For an ideal gas, the species molar volume (m³/mol) is the same for all species:

$$\frac{M_i}{\rho_i} = \frac{R_g T}{p} \quad (3-9)$$

so that:

$$v_p = \frac{R_g T}{p} \sum_j \sum_i v_{ij} r_j V_r. \quad (3-10)$$

The energy balance for an ideal reacting gas is:

$$V_r \sum_i c_i C_{p,i} \frac{dT}{dt} = w_s + Q + Q_{\text{ext}} + V_r \frac{dp}{dt} + \sum_i v_{f,i} c_{f,i} (h_{f,i} - h_i) \quad (3-11)$$

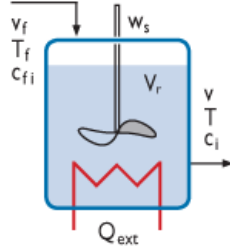
For an incompressible and ideally mixed reacting liquid, the energy balance is:

$$V_r \sum_i c_i C_{p,i} \frac{dT}{dt} = w_s + Q + Q_{\text{ext}} + \sum_i v_{f,i} c_{f,i} (h_{f,i} - h_i) \quad (3-12)$$

Find the balance equations displayed the **Equations** area, when selecting the **Mass Balance** or **Energy Balance** page, respectively.

The CSTR with Constant Volume

The continuous stirred tank reactor (CSTR) has reacting species entering and leaving the reactor by means of feed and outlet streams. The reactor is once again assumed to be perfectly mixed, so that the species concentrations of the exit stream are the same as the concentrations in the reactor volume.



The species mass balances are given by:

$$\frac{d(c_i V_r)}{dt} = v_{f,i} c_{f,i} - v c_i + R_i V_r \quad (3-13)$$

where v is the volumetric flow rate (m^3/s) of the outlet stream. Assuming constant reactor volume:

$$\frac{dV_r}{dt} = 0 \quad (3-14)$$

and setting the volumetric flow rate to:

$$v = \sum v_{f,i} + v_p \quad (3-15)$$

Equation 3-13 can be rewritten as:

$$V_r \frac{dc_i}{dt} = v_{f,i} c_{f,i} - \left(\sum v_{f,i} + v_p \right) c_i + R_i V_r \quad (3-16)$$

The volumetric production rate is labeled v_p (m^3/s), and is expressed by Equation 3-8 for ideally mixed liquids and by Equation 3-10 for ideal gases.

The energy balance for an ideal reacting gas is:

$$V_r \sum_i c_i C_{p,i} \frac{dT}{dt} = w_s + Q + Q_{\text{ext}} + V_r \frac{dp}{dt} + \sum_i v_{f,i} c_{f,i} (h_{f,i} - h_i) \quad (3-17)$$

For an incompressible and ideally mixed reacting liquid, the energy balance is:

$$V_r \sum_i c_i C_{p,i} \frac{dT}{dt} = w_s + Q + Q_{\text{ext}} + \sum_i v_{f,i} c_{f,i} (h_{f,i} - h_i) \quad (3-18)$$

You find the mass balance given by Equation 3-16 displayed in the **Equations** area, when the **Mass Balance** page is active. The energy balance given by Equation 3-17 or Equation 3-18 is displayed when the **Energy Balance** page is active.

The CSTR with Constant Mass

This reactor model assumes that the outlet feed is adjusted in such a way that the total mass of the reactor is held constant.

As before, the species mass balances for the CSTR are given by:

$$\frac{d(c_i V_r)}{dt} = v_{f,i} c_{f,i} - v c_i + R_i V_r \quad (3-19)$$

The reactor volume as a function of time is given by:

$$\frac{dV_r}{dt} = \sum v_{f,i} - v + v_p \quad (3-20)$$

The volumetric flow rate of the outlet stream, v (m³/s), is set to:

$$v = \frac{\sum v_{f,i}}{\rho_f} \quad (3-21)$$

The energy balance for an ideal reacting gas is:

$$V_r \sum_i c_i C_{p,i} \frac{dT}{dt} = w_s + Q + Q_{\text{ext}} + V_r \frac{dp}{dt} + \sum_i v_{f,i} c_{f,i} (h_{f,i} - h_i) \quad (3-22)$$

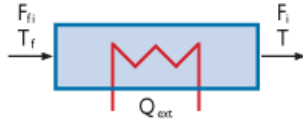
For an incompressible and ideally mixed reacting liquid, the energy balance is:

$$V_r \sum_i c_i C_{p,i} \frac{dT}{dt} = w_s + Q + Q_{\text{ext}} + \sum_i v_{f,i} c_{f,i} (h_{f,i} - h_i) \quad (3-23)$$

You find the balance equations displayed in the **Equations** area, when selecting the **Mass Balance** or **Energy Balance** page, respectively.

The Plug-Flow Reactor

In the plug-flow reactor, the species concentrations and the temperature vary with position. For a tubular reactor configuration, concentration and temperature gradients are allowed to develop in the axial direction, but not in the radial direction,



The species mass balances are given by:

$$\frac{dF_i}{dV} = R_i \quad (3-24)$$

where F_i is the species molar flow (mol/s), V is the reactor volume (m^3) and R_i denotes the species rate expression ($\text{mol}/(\text{m}^3 \cdot \text{s})$).

In order to evaluate the rate expressions R_i , which are functions of the species concentrations, Reaction Engineering Lab calculates:

$$c_i = \frac{F_i}{v} \quad (3-25)$$

where v is the volumetric flow rate (m^3/s).

For ideal gases:

$$v = \frac{R_g T}{p} \sum_i F_i \quad (3-26)$$

so that

$$c_i = \frac{p}{R_g T} \frac{F_i}{\sum_i F_i} \quad (3-27)$$

For liquids, the volumetric flow rate is given by:

$$v = \frac{\rho_0 v_0}{\rho} \quad (3-28)$$

Neglecting pressure drop, the energy balance for an ideal reacting gas, as well as an incompressible and ideally mixed reacting liquid is:

$$\sum_i F_i C_{p,i} \frac{dT}{dV} = w_s + Q + Q_{\text{ext}} \quad (3-29)$$

where $C_{p,i}$ is the species molar heat capacity (J/(mol·K)), and w_s represents an additional work term, for instance the shaft work per volume (J/(m³·s)). Q_{ext} is the heat added to the system per unit volume (J/(m³·s)), and Q denotes the heat due to chemical reaction (J/(m³·s)).

$$Q = -\sum_j H_j r_j \quad (3-30)$$

where H_j the heat of reaction (J/mol), and r_j the reaction rate (mol/(m³·s)).

You find the mass balance given by Equation 3-24 displayed in the **Equations** area, when the **Mass Balance** page is active. The energy balance given by Equation 3-29 is displayed when the **Energy Balance** page is active.

Below the reactor type list, you find the following selections:

- Reacting fluid
- Calculate thermodynamic properties
- Calculate species transport properties
- Include energy balance

In the **Reacting fluid** list you specify the phase of the reaction fluid as a **gas** or **liquid**. Reacting fluids in the gas phase are treated as ideal gases while liquids are considered incompressible ideal mixtures. The choice of fluid phase affects the set of predefined expressions made available in edit fields, defining thermodynamic as well as transport properties. Note that you can, for example, include a solid catalyst phase in the model

using the free catalyst site concentration as a variable. However, in such a case you have to exclude variables describing the solid phase from the calculation of the fluid properties. It is also possible to mix liquids and gases in the Reaction Engineering Lab, but you have to specify the mixture properties by changing the predefined expressions for density and heat capacity.

To add an energy balance to the model, select the **Calculate thermodynamic properties** check box and then the **Include energy balance** check box. In the cases when you want to calculate transport properties, select the **Calculate species transport properties** check box.

The right hand side of the **Model Settings** dialog box displays the following six pages:

- General
- Mass Balance
- Energy Balance
- Feed Streams
- Stoichiometry
- Init

On these pages you enter *reactor specific* settings, for instance the temperature and pressure conditions, and the number of feed streams. To fully characterize a reactor model you also need to provide *species specific* information, such as starting concentrations and thermodynamic properties. Such setting are entered in the Species interface in the **Reaction Settings** dialog, as described under Reaction Settings—Species Interface on page 82.

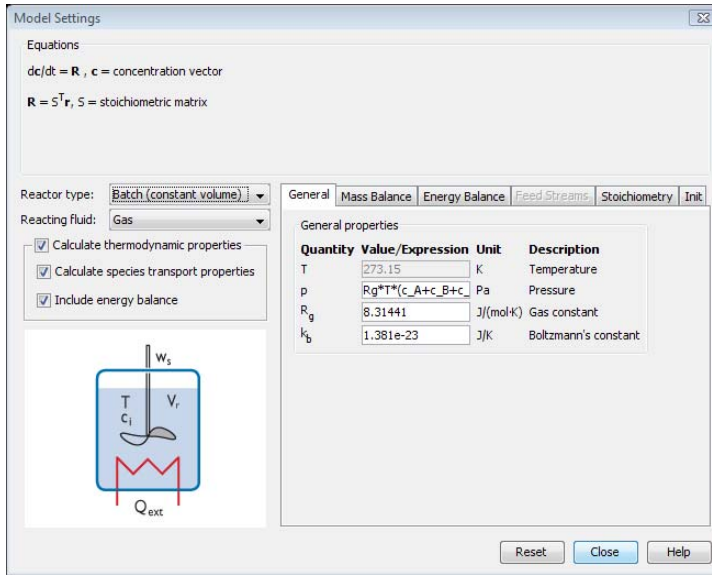


Figure 3-5: The General page displayed in the Model Settings dialog box.

The four edit fields on the **General** page contain parameters used in predefined expressions defined in the Reaction Engineering Lab. If your system is isothermal, or if you use a predefined temperature as a function of time, you do not need to set up an energy balance. In such cases, the value of the temperature **T** is used by the Reaction Engineering Lab to evaluate all temperature-dependent expressions in the material balances (when an energy balance is not included in the simulation). In the **T** edit field you can enter a number (298.15), variable name (**T_0**), or an expression of time, t (for example, $298.15 + 5 \cdot \sin(2 \cdot \pi \cdot t / (3600 \cdot 24))$). If you are also setting up an energy balance for the system, temperature is a dependent variable along with the concentrations in the system of equations, and the **T** edit field is made unavailable by the Reaction Engineering Lab.

In the cases when the kinetic model does not require an energy balance, the Reaction Engineering Lab only uses the pressure value **p** for calculating transport properties. These properties are used in the export to space-dependent models in COMSOL Multiphysics. The default value in the **p** edit field is

$$p = R_g T \sum c_i \quad (3-31)$$

for gas phase systems, and 101,325 Pa for liquid phase systems.

Finally, the ideal gas constant R_g and Boltzmann's constant, k_b , are provided for reference, as these are used in certain predefined expressions.

The Mass Balance Page

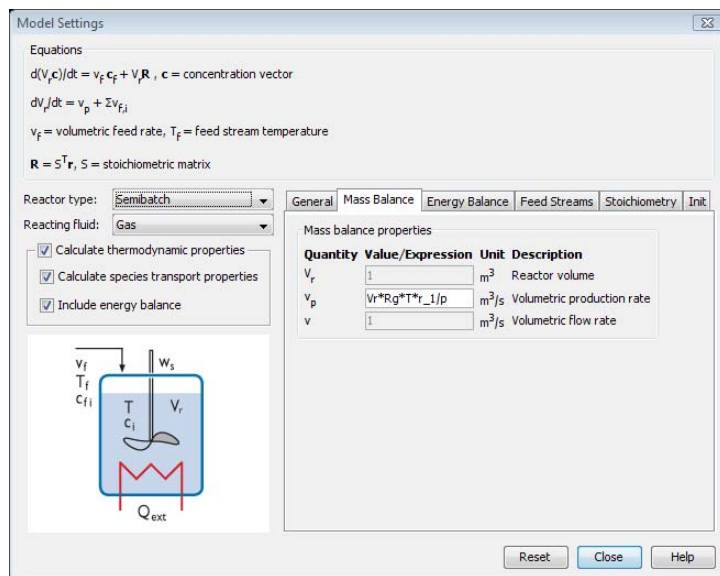


Figure 3-6: The Mass Balance page displayed in the Model Settings dialog box.

The **Mass Balance** page supplies parameters and expressions for the species mass balance equations displayed in the **Equations** area, at the top of the **Model Settings** dialog box. The edit fields for the system volume (V_r), the volumetric production rate (v_p) and the volumetric flow rate (v) are available depending on the selection of reactor type. You can edit the V_r edit field when modeling the **Batch**, **Batch (constant volume)** and **CSTR (constant volume)** types. As the balance equations of the **Batch** reactor type accounts for changing volume, you may enter time dependent volume expressions in the V_r field. The v_p edit field is available when modeling **Semibatch** or **CSTR** reactors. For liquid phase reactions, the edit field contains the predefined expression:

$$v_p = \sum_j \sum_i v_{ij} \frac{M_i}{\rho_i} r_j V_r \quad (3-32)$$

Reaction Engineering Lab automatically inserts the stoichiometric coefficient (v_{ij}) and expressions for the reaction rates (r_j), as defined in the Reaction interface of the **Reaction Settings** dialog. Furthermore, the values of the molecular weight (M_i) and the species density (ρ_i) are automatically taken from Species interface of the **Reaction Settings** dialog. It follows that the $\mathbf{v_p}$ edit field may be empty if, for instance, no reaction has been specified in the **Reaction Settings** dialog. Set the $\mathbf{v_p}$ edit field to zero if you want to ignore volume changes due to reaction.

For gas phase reactions, the $\mathbf{v_p}$ edit field contains the predefined expression:

$$v_p = \frac{R_g T}{p} \sum_j \sum_i v_{ij} r_j V_r. \quad (3-33)$$

You can edit the \mathbf{v} edit field when modeling with the **CSTR (constant mass)** or **Plug-flow** reactor types. For gas phase reactions, modeled with the **Plug-flow** reactor, the \mathbf{v} edit field contains the following predefined expression:

$$v = \frac{R_g T}{p} \sum_i F_i \quad (3-34)$$

For liquid phase reactions, default settings assume constant fluid density, and consequently a constant volumetric flow throughout the reactor:

$$v = \frac{\rho_0 v_0}{\rho} \quad (3-35)$$

The default value in the \mathbf{v} edit field is one.

You are free to enter an expression on the form of Equation 3-35 in order to account for varying density.

Note that all predefined constants and expressions provided in edit fields may be overwritten by user-defined expressions. This allows you to go beyond the modeling assumptions that are default in Reaction Engineering Lab. For further reading on the specific mass balances and volumetric rates, see the beginning of the section Model Settings on page 55.

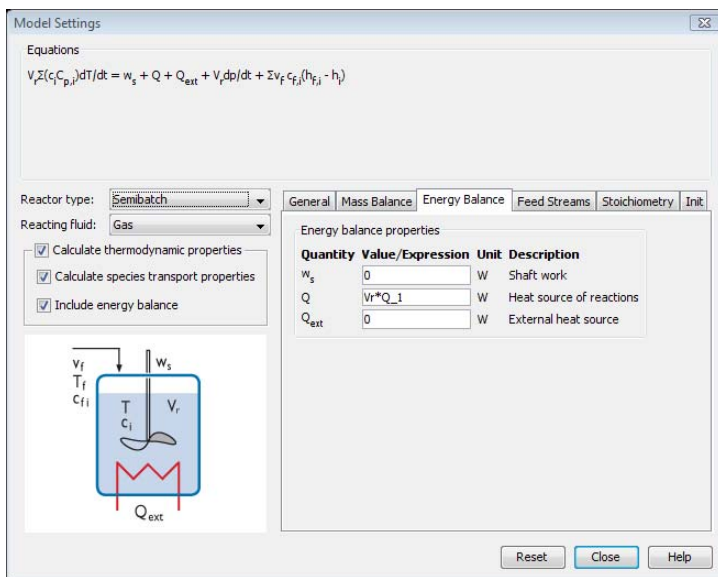


Figure 3-7: The Energy Balance page displayed in the Model Settings dialog box.

To access the **Energy Balance** page you first need to select the **Calculate thermodynamic properties** check box and the **Include energy balance** check box. The **Energy Balance** page supplies parameters and expressions for the energy balance equations displayed in the **Equations** area, at the top of the **Model Settings** dialog box.

The edit fields for the shaft work (w_s), heat source of reaction (Q), and external heat source (Q_{ext}), are all available for any given reactor type. The default value for w_s and Q_{ext} is zero. The Q edit field holds the following predefined expression for the **Batch**, **Semibatch** and **CSTR** reactor types:

$$Q = -V_r \sum_j H_j r_j \quad (3-36)$$

Reaction Engineering Lab automatically inserts expressions for the enthalpy of reaction (H_j) and the reaction rate (r_j), as defined in the Reaction Settings dialog.

For the **Plug-flow** reactor the heat source of reactions given as:

$$Q = -\sum_j H_j r_j \quad (3-37)$$

For further reading on the specific energy balances corresponding source terms, see the beginning of the section Model Settings on page 55.

The Feed Streams Page

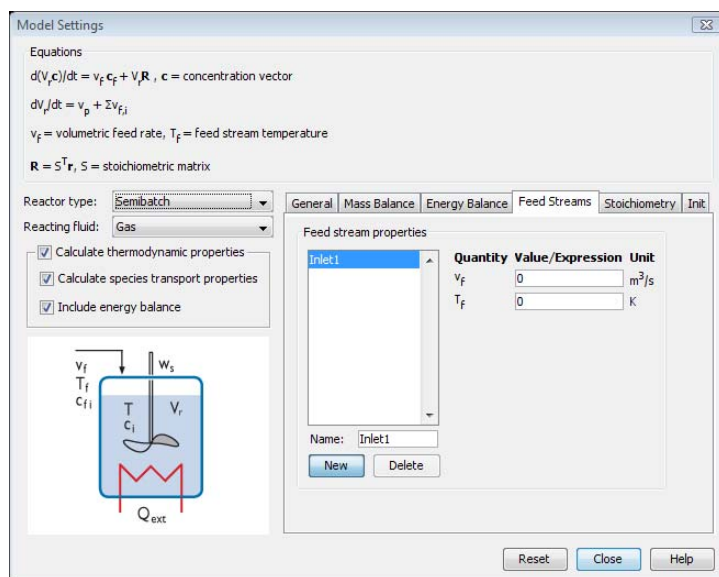


Figure 3-8: The Feed Streams page displayed in the Model Settings dialog box.

The **Feed Streams** page is available for the **Semibatch** and **CSTR** reactor types. On this page you define the number and properties of the feed streams supplying the reactor with chemicals. Create one or more feed streams by clicking the **New** button. Editing the **Name** edit field allows you to label each stream as desired. To specify the volumetric feed rate ($\mathbf{v_f}$) and feed stream temperature ($\mathbf{T_f}$), first select an entry in the feed streams list and then enter the corresponding values in the $\mathbf{v_f}$ and $\mathbf{T_f}$ edit fields. The individual species are assigned to the inlet streams in the Species interface in the **Reaction Settings** dialog (see “Reaction Settings—Species Interface” on page 82).

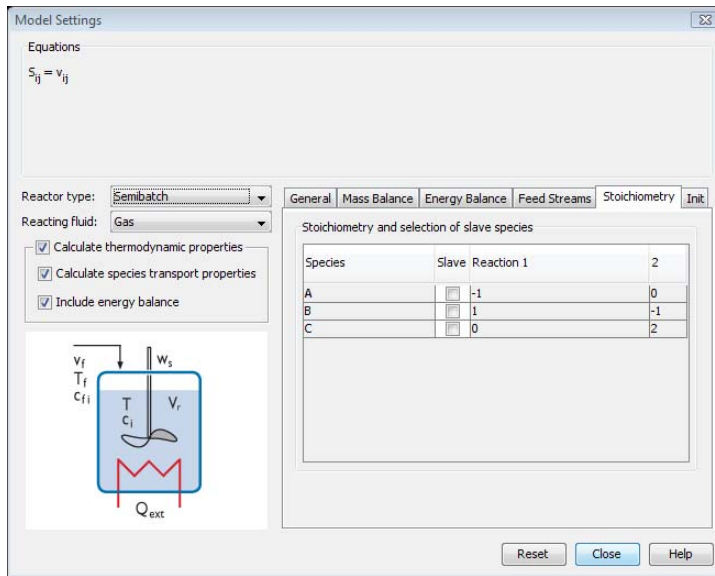


Figure 3-9: The Stoichiometry page displayed in the Model Settings dialog box.

The **Stoichiometry and selection of slave species** area displays a stoichiometric matrix that lists chemical reactions as columns and the involved species as rows. Stoichiometric coefficients in the matrix elements are defined as being negative for reactants and positive for products. The column labeled **Slave** holds check boxes that are used only for equilibrium reactions. In most cases, there is no need to modify the setting of the **Stoichiometry** page.

To illustrate the **Slave** species concept, consider the following example. Two nonequilibrium reaction are taking place in a perfectly mixed isothermal batch reactor of constant volume:



The corresponding mass balances are:

$$\frac{d}{dt}c_A = -r_1 \quad (3-40)$$

$$\frac{d}{dt}c_B = r_1 - r_2 \quad (3-41)$$

$$\frac{d}{dt}c_C = 2r_2 \quad (3-42)$$

Figure 3-9 shows the corresponding stoichiometric matrix displayed on the **Stoichiometry** page.

Now compare Equation 3-40 through Equation 3-42 with the balance equations that Reaction Engineering Lab sets up for the related chemistry, where the second reaction is now at equilibrium:



In contrast to the reversible reaction given by Equation 3-39, the explicit forward and reverse reaction rates of the equilibrium reaction (Equation 3-44) are not known. To make use of the information contained in the equilibrium relation, the mass balances must be reformulated. Linear combinations of rate expressions remove the unknown forward and reverse reaction rates of Equation 3-44. Furthermore, the equilibrium expression is added to the new set of material balances. Mass balances set up for the reactions given by Equation 3-43 and Equation 3-44 are then:

$$\frac{d}{dt}c_A = -r_1 \quad (3-45)$$

$$\frac{d}{dt}(2c_B + c_C) = 2r_1 \quad (3-46)$$

$$K_2^{eq} = \frac{c_C^2}{c_B}. \quad (3-47)$$

The equilibrium expression (Equation 3-47) introduces an algebraic relationship between the species' concentrations. In order to satisfy this relationship, one species' concentration must be directly linked to the other's. The dependent species is known

as the *slave species*, and the Reaction Engineering Lab highlights it by selecting its check box in the **Slave** column of the stoichiometric matrix (see Figure 3-10).

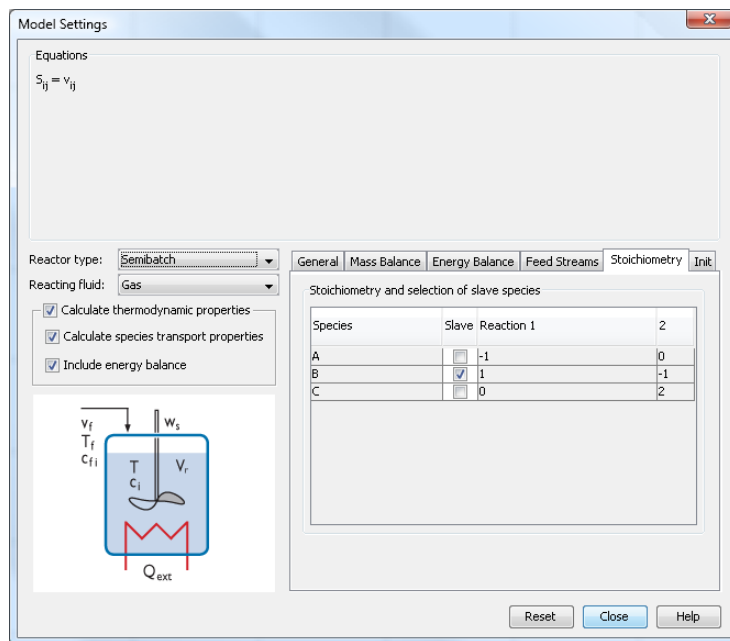


Figure 3-10: The Stoichiometry page displayed for a reaction set containing an equilibrium reaction, where a slave species (B) has been selected automatically.

The default solver settings automatically computes the initial concentration of the slave species from the initial concentrations of the other (non-slave) species and the equilibrium expression.

The Reaction Engineering Lab automatically performs the procedure of eliminating equilibrium reaction rates from material balances, and it does so for any number of equilibrium reactions in a reaction set. Furthermore, the selection of slave species is automatic. It is possible to change the default selection of slave species by clearing and selecting the check boxes in the stoichiometric matrix.

When you export a reaction model from the Reaction Engineering Lab to the Chemical Engineering Module, the corresponding mass balances—now partial differential equations—undergo the same automatic elimination process. In the Chemical Engineering Module application modes generated in the export process, the stoichiometric matrix and the selection of slave species appear in a noneditable form.

If you want to change the selection of slave species for the application modes, you must make these changes in the Reaction Engineering Lab and then re-export the model.

For more reading on how Reaction Engineering Lab treats reaction kinetics and chemical equilibrium, see “The Kinetics Page” on page 75.

The Initial Values Page

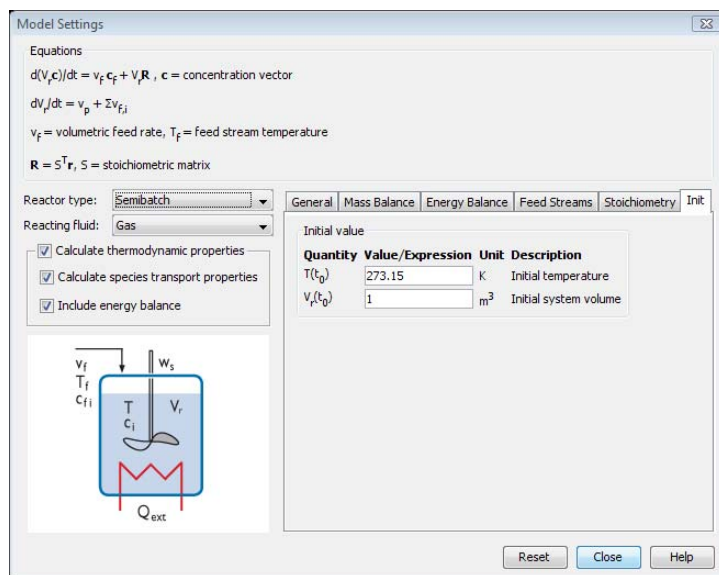


Figure 3-11: The Init page displayed in the Model Settings dialog box.

The **Init** page supplies initial values for the balance equations solved by Reaction Engineering Lab. If an energy balance is included in the model you supply the initial reactor temperature in the **T(t₀)** edit field. For the **Plug-flow** reactor type, enter the inlet temperature in the **T(V₀)** edit field. The edit field for the initial system volume (**V(t₀)**) is available for the **Semibatch** and **CSTR (constant mass)** reactor models.

Reaction Settings—Reactions Interface

Choose **Model>Reaction Settings** and click the **Reactions** tab to bring up the Reactions interface (Figure 3-12). Its main components are the **Reaction selection** list, the **Kinetics** page, and the **Thermo** page.

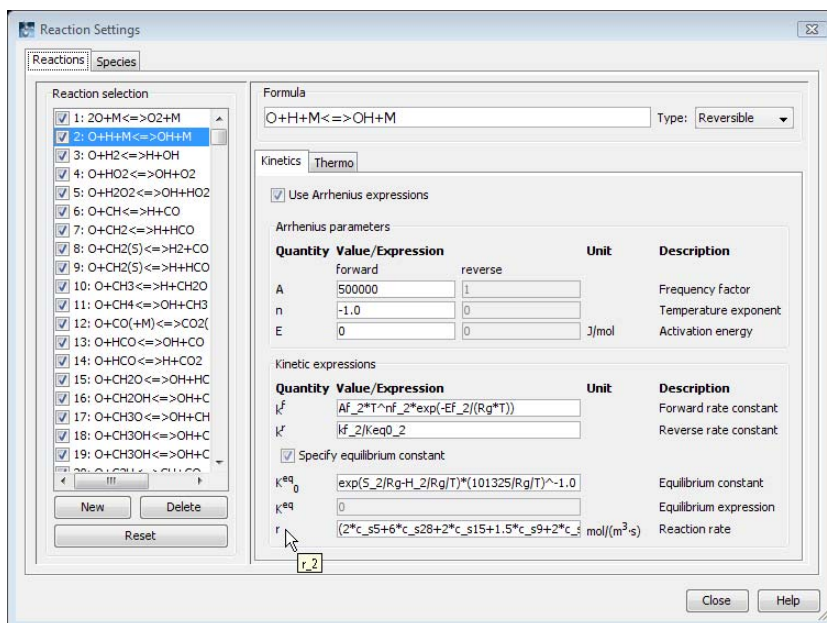


Figure 3-12: The Reactions interface, featuring the Reaction selection list (left) the Formula edit field (top), and the Kinetics page (right).

The Reactions interface contains the **Reaction selection** list, where reactions appear when you enter chemical reaction formulas in the **Formula** edit field. To create new entries, click the **New** button and then enter a chemical reaction formula in the **Formula** edit field; remove unwanted entries with the **Delete** button. To edit a reaction formula, select the appropriate entry in the **Reaction selection** list and change the expression in the **Formula** edit field. The Reaction Engineering Lab examines the species taking part in the model's reactions and automatically arranges them in a corresponding **Species selection** list (see the description that follows shortly).

Valid species names consist of a case-sensitive combination of letters, numbers, and “+” or “-” signs. With the exception of the “+” and “-” signs, which are used for ions, special characters are not allowed as species names or part of species names (for example, (), [], *, #, and _). In addition, the first character in a species name has to be a letter to avoid confusion with the stoichiometric coefficients in the reaction formula. Ions are labeled with one plus or minus sign per species charge added directly after the species name. For example, A++ represents a cationic monomer with a twofold positive charge; A2+ represents a cationic dimer of species A with a single positive charge; and 2A+ represents two cationic monomers, each with a single positive charge. This automatically fills in the charge of the species ion the **Charge** edit field in the Species interface.

For each reaction formula you enter, specify the reaction type with a delimiter separating the two sides of the equation: <=> denotes a reversible reaction; => denotes an irreversible reaction; and = denotes a reaction at chemical equilibrium.

It is possible to change the reaction type either by editing the expression in the **Formula** edit field or by selecting an entry in the **Reaction selection** list and then changing the selection in the **Type** list. The **Type** list also displays the current setting for the selected reaction (reversible, irreversible, or equilibrium).

The check boxes at the left of the reactions in the **Reaction selection** list allow for easy activation/deactivation of selected reactions. Creating reaction subsets in this manner provides a straightforward approach to investigating the influence of individual reactions on the overall reaction system. Species that take part only in deactivated reactions are automatically deactivated in the **Species selection** list. Furthermore, if you delete reactions from the **Reaction selection** list, the Reaction Engineering Lab automatically deletes from the **Species selection** list those species that take part only in the deleted reactions.

When you enter chemical formulas, each reaction is associated with a unique identification number. Note that this is not a row number but rather an absolute reference number to a given reaction. This means that a reaction keeps its identification number, even if you delete reactions with a lower number. Furthermore, constants and expressions within edit fields associated with a given reaction are also indexed with the reaction number (see the labeling rules in the following section).

As a general labeling rule, the variable name referring to the contents of an edit field associated with an entry in the **Reaction selection** list is given by the edit field’s name indexed by the reaction number. For example, if you select the entry for Reaction 1 from the **Reaction selection** list, then the contents of the rate constant edit fields **k^f** and

k^r are labeled k_1^f and k_1^r , respectively. You can use these variables—typed as `kf_1` and `kr_1`, respectively—in the expressions of other edit fields. Continuing the example, the predefined reaction rate expression in the **r** edit field, labeled r_1 , is a function of the rate constants k_1^f and k_1^r . Assume that you overwrite the expression in the **r** edit field with the expression `r_4`; then the Reaction Engineering Lab interprets this as r_1 being equal to r_4 , the expression appearing in the **r** edit field when Reaction 4 is selected.

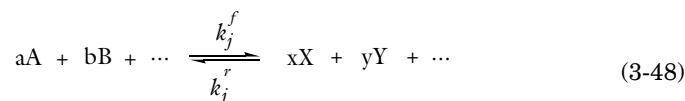
The purpose of the identification number for each reaction and the labeling rules is to allow you to create arbitrary relations for the reaction rates and rate constants in different reactions. For example, if you would like to keep a constant relation between the rates of different reactions, you can use the above labeling and indexing to express this directly in the edit fields.

The variable names of all edit fields in the **Reactions** interface appear in the Chapter 5, “Reference Section.” Furthermore, the variable names associated with a particular edit field appear when you place the mouse cursor on top of the edit field’s name. This is exemplified in Figure 3-12. When the second entry is selected in the **Reaction selection** list, and the cursor is placed over the **r** symbol, the tooltip `r_2` appears.

The Kinetics Page

The layout of the **Kinetics** page appears in Figure 3-12; this page contains information about the kinetics of a selected reaction. You can select to specify the kinetic input data by entering the rate constants directly, for isothermal reactions, or you can specify the activation energy and the frequency factor in the Arrhenius expressions to account for temperature variations. Select the **Use Arrhenius expressions** check box to access the appropriate edit fields.

Consider a general reaction belonging to a set of j reactions and involving i species:



For such a reaction set, the reaction rates r_j (mol/(m³.s)), can be described by the mass action law:

$$r_j = k_j^f \prod_{i \in \text{react}} c_i^{-v_{ij}} - k_j^r \prod_{i \in \text{prod}} c_i^{v_{ij}}. \quad (3-49)$$

Here, k_j^f and k_j^r denote the forward and reverse rate constants, respectively. The concentration of species i is denoted as c_i (mol/m³). The stoichiometric coefficients are denoted ν_{ij} , and are defined as being negative for reactants and positive for products. In practice, a reaction seldom involves more than two species colliding in a reacting step, which means that a kinetic expression is usually of order 2 or less (with respect to the involved concentrations).

In addition to the concentration dependence, you can include the temperature dependence of reaction rates by using the predefined Arrhenius expressions for the rate constants:

$$k = AT^n \exp\left(-\frac{E}{R_g T}\right). \quad (3-50)$$

To activate the **Arrhenius parameters** area and make the kinetic expressions use these parameters, select the **Use Arrhenius expressions** check box. In the **Arrhenius parameters** area, A denotes the frequency factor, n the temperature exponent, E the activation energy (J/mol) and R_g the gas constant, 8.314 J/(mol·K). The pre-exponential factor, including the frequency factor A and the temperature factor T^n , is given the units (m³/mol) ^{$\alpha-1$} /s, where α is the order of the reaction (with respect to the concentrations). Edit fields are available for each of the Arrhenius parameters in the equation above.

For an **Irreversible** reaction, predefined expressions appear in the edit fields for the **Forward rate constant**, k_f , and the **Reaction rate**, r . In the **Arrhenius parameters** area, the Reaction Engineering Lab fills in the edit fields **A**, **n**, and **E**, all pertaining to the forward rate constant, with default values and makes the remaining fields unavailable.

The reaction rate edit field r displays the reaction rate expression for the selected reaction according to the mass action law. You can overwrite any of the predefined expressions with your own expressions or constants. For example, the concentrations of species A and B are labeled c_A and c_B by the Reaction Engineering Lab. You can type any expression of these variables—entered as c_A and c_B , respectively—in the r edit field to overwrite the default mass action law expression (it does not have to be a power-law expression, but can be any analytical expression). Should you want to revert to the predefined expressions given for a specific reaction, select the reaction entry in the **Reaction selection** list and click the **Reset** button.

For a **Reversible** reaction, predefined expressions appear in the edit fields for the **Forward rate constant**, k^f , the **Reverse rate constant**, k^r , and the **Reaction rate**, r . In the **Arrhenius parameters** area, the Reaction Engineering Lab fills in the edit fields **A**, **n**, and

E, all pertaining to the forward and reverse rate constants, with default values. As mentioned in the above paragraph, you can overwrite any of the predefined expressions with custom expressions of the modeled concentrations, temperature, and model constants.

The edit field for the equilibrium constant, K^{eq}_0 , is also available, filled in with the predefined expression

$$K^{eq}_{0,j} = \exp\left(-\frac{H_j}{R_g T} + \frac{S_j}{R_g}\right). \quad (3-51)$$

The exponential term in Equation 3-51 as being related to the Gibbs free energy of reaction, G_j (J/mol):

$$G_j = H_j - TS_j. \quad (3-52)$$

The thermodynamic expressions for H_j and S_j are described in detail shortly. In the case of reversible reactions, it is also possible to make use of equilibrium relationships in order to indirectly calculate reaction constants. For instance, you can calculate the reverse rate constant from the equilibrium condition in this way:

$$k^r = \frac{k^f}{K^{eq}} \quad (3-53)$$

Consider an example implementing the form of Equation 3-53 for the reverse rate constant: For a hypothetical Entry 1 in the **Reaction selection** list, the Arrhenius expression in the reverse rate constant edit field, k^r , would simply be overwritten by the expression $kf_1/Keq0_1$.

When using Equation 3-53, take care to ensure that the equilibrium constant has the proper units. If K^{eq}_0 is derived from gas-phase data, thus being expressed in pressure units, you must provide the proper conversion with the relationship

$$K^{eq}_{c,j} = K^{eq}_{p,j} \left(\frac{1}{R_g T}\right)^{\sum_{i=1} v_{ij}} \quad (3-54)$$

where $K^{eq}_{c,j}$ is the equilibrium constant expressed in concentration units, $K^{eq}_{p,j}$ is the equilibrium constant expressed in pressure units, and v_{ij} are the stoichiometric coefficients defined as being positive for reactants and negative for products.

For an **Equilibrium** reaction, only the equilibrium constant edit field, K^{eq}_0 , and the equilibrium expression field, K^{eq} , are available. In the K^{eq} field, you can overwrite the predefined expression corresponding to Equation 3-51 with an arbitrary expression of the concentrations and temperature. The default settings for the reaction given by Equation 3-48 and assuming equilibrium, yields the expression for the equilibrium expression in Equation 3-55:

$$K^{eq} = \frac{c_X^x c_Y^y \dots}{c_A^a c_B^b \dots} \quad (3-55)$$

The following short example illustrates how the Reaction Engineering Lab handles equilibrium reactions in the formulation of the material balance equations. Consider the reaction



According to Equation 3-49 the reaction rate (mol/(m³·s)) is formulated as

$$r = k^f c_A - k^r c_B \quad (3-57)$$

where c_A and c_B are the concentrations (mol/m³) of A and B , and k^f and k^r are the forward and reverse rate constants (1/s), respectively. The net rate expressions with respect to species A and B are then

$$R_A = -k^f c_A + k^r c_B = -r \quad (3-58)$$

$$R_B = k^f c_A - k^r c_B = r \quad (3-59)$$

Writing down the material balances for species A and B , respectively, yields:

$$\frac{\partial c_A}{\partial t} + \nabla \cdot \mathbf{N}_A = R_A = -r \quad (3-60)$$

$$\frac{\partial c_B}{\partial t} + \nabla \cdot \mathbf{N}_B = R_B = r \quad (3-61)$$

where \mathbf{N}_A and \mathbf{N}_B are the molar flux vectors (mol/(m²·s)) for species A and B , respectively. The rate of consumption of species A equals the production rate of species B , as shown in Equation 3-60 and Equation 3-61. Assuming the reaction in

Equation 3-56 is at equilibrium, a dilemma arises because r is not known explicitly. However, the relationship between the forward and reverse reaction rates in Equation 3-56 is given by the following ratio:

$$K^{\text{eq}} = \frac{k^f}{k^r} = \frac{c_B}{c_A} \quad (3-62)$$

With the combined information in Equation 3-60 through Equation 3-62, the Reaction Engineering Lab is able to define the mass balances for the equilibrium system without explicitly knowing the reaction rate expressions. The Reaction Engineering Lab eliminates the reaction rate terms by linearly combining the mass balances so that the equation system becomes

$$\frac{\partial}{\partial t}(c_A + c_B) + \nabla \cdot (\mathbf{N}_A + \mathbf{N}_B) = 0 \quad (3-63)$$

$$K^{\text{eq}} = \frac{c_B}{c_A}. \quad (3-64)$$

The Reaction Engineering Lab solves these equations directly. In general, for a system of reactions contributing to n mass balances and with m reactions being at equilibrium, the reduced system of equations to be solved would be composed of $n-m$ mass balances and m equilibrium expressions. The elimination process producing the above system of equations is automated in the Reaction Engineering Lab, allowing you to effortlessly include chemical equilibrium conditions, even for very complicated reaction models.

The system of equations given by Equation 3-63 and Equation 3-64, includes the flux vectors of the respective species, \mathbf{N}_A and \mathbf{N}_B , with the corresponding transport properties. The Reaction Engineering Lab formulates such a system only for space-dependent problems, which you can solve through the export to COMSOL Multiphysics.

The Thermo Page

The **Thermo** tab is only available when you have selected the **Calculate thermodynamic properties** check box in the **Model Settings** dialog box (see Figure 3-4). The

Reactions>Thermo page (Figure 3-13) contains information about thermodynamic properties related to a selected reaction.

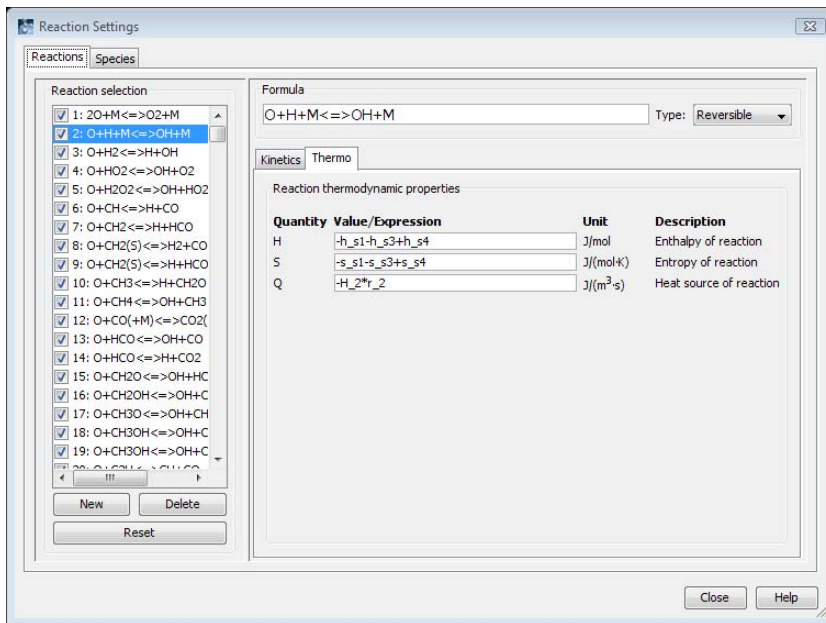


Figure 3-13: The Thermo page as shown in the Reactions interface.

The enthalpy of reaction (J/mol) is calculated by the Reaction Engineering Lab from species properties and the related stoichiometric coefficients in this way:

$$H_j = \sum_i v_{ij} h_i. \quad (3-65)$$

Similarly, the entropy of reaction (J/(mol·K)) comes from the relationship

$$S_j = \sum_i v_{ij} s_i. \quad (3-66)$$

In these equations, h_i and s_i are the species' molar enthalpy (J/mol) and entropy (J/(mol·K)), respectively. You enter these quantities on the **Species>Thermo** page either by using the predefined polynomial or by providing a custom expression or constants. The stoichiometric coefficients, v_{ij} , are defined as being negative for reactants and positive for products. As noted earlier, using Equation 3-65 and Equation 3-66 to equate the Gibbs free energy of reaction enables you to express the equilibrium

constant according to Equation 3-51. The expression for the equilibrium constant goes into the edit field K^{eq}_0 of the **Kinetics** page (described earlier).

The heat source of reaction (J/(m³·s)) is given as:

$$Q_j = -H_j r_j. \quad (3-67)$$

The sum of Q_j over all reactions is the total heat source due to chemical reaction:

$$Q = \sum_j Q_j. \quad (3-68)$$

This term appears in the **Model Settings>Energy Balance** dialog box.

Reaction Settings—Species Interface

Clicking the **Species** tab in the **Reaction Settings** dialog brings up the Species interface (Figure 3-14). The main components of the Species interface are the **Species** selection list, the **General** page, the **Feed Stream** page, the **Thermo** page, and the **Transport** page. The **Feed Stream** tab is only available when you have selected one of the **Reactor types**; **Semibatch**, **CSTR** or **Plug-flow**. The **Thermo** tab is only available when you have selected the **Calculate thermodynamic properties** check box while the **Transport** tab is available when you select the **Calculate species transport properties** check box. All the above selection are made in the **Model Settings** dialog box (Figure 3-4).

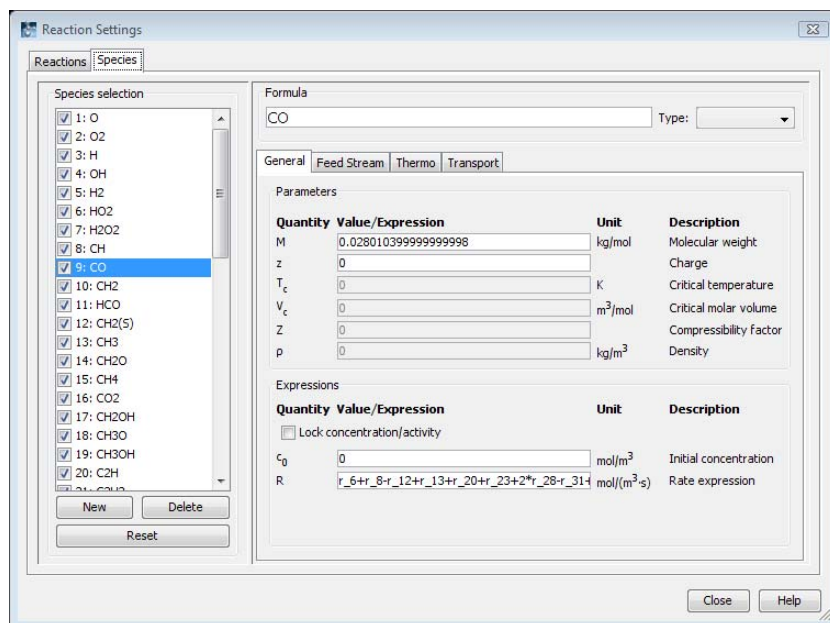


Figure 3-14: The default Species interface in the Reaction Engineering Lab featuring the Species selection list (left) and the General page (right).

The Reaction Engineering Lab generates the **Species** selection list based on the chemical reaction formulas entered into the **Reaction** selection list.

A general rule applies to the labeling of variables referring to the contents of edit fields: variables names consist of the edit field's name indexed by the species name. For instance, the species rate expression, which appears in the **R** edit field, is labeled **R_h2o**

for the species named h2o. Moreover, Cp_h2o is the heat capacity, eta_h2o is the viscosity, and so on.

Chapter 5, “Reference Section,” lists the variable names of all edit fields. In addition, the variables associated with a particular edit field appear when you hold the mouse cursor on top of the edit field’s name. This system of reference, which is parallel for both the Reactions and Species interfaces, makes it straightforward to interpret the contents of edit fields and also to see how the fields interrelate.

Just as with entries in the **Reaction selection** list, you can add, remove, or deactivate entries in the **Species selection** list. Deactivation of a species automatically deactivates any reactions in which the species participates. Before you can delete a species, a warning prompts you that reactions including the species will also be removed.

For each species you enter, it is possible to change its characteristics by making a selection in the **Type** list. You can here specify the special cases when a species serves as the solvent in a solution or when a species is at steady state. The selection of a species as solvent has implications in the calculation of thermodynamic and transport properties. These properties are also used in the export to the Chemical Engineering Module, and you have to select different application modes if you intend to apply a solvent-solute approximation or if you want to apply a full multicomponent description for the reacting fluid.

The default settings in the Reaction Engineering Lab implement the description for multicomponent fluids. This means that it generates the mixture’s physical properties dependent upon its composition. This default choice is a prerequisite for the use of the multicomponent mass balance formulations in the Chemical Engineering Module (Maxwell-Stefan Diffusion and Convection) of COMSOL Multiphysics.

Configuring a species as a solvent sets the physical properties of the reacting fluid equal to those of the solvent species; specifically, its density, heat capacity, viscosity, and thermal conductivity. Furthermore, the Reaction Engineering Lab implements a solute-solvent approximation for the interaction of species in the fluid and describes their transport properties accordingly. In material balances this means that the diffusion coefficient is independent of any of the solute’s concentrations, because every solute only interacts with solvent molecules, regardless of their concentration. In addition, the convective term in the flux of species is directly given by the velocity field of the solvent multiplied by the solute concentration. Select a **Solvent** species when making use of the mass balance formulations in the Diffusion and the Convection and Diffusion application modes in the Chemical Engineering Module of COMSOL Multiphysics.

A solvent can furthermore affect the reaction kinetics. Select **Solvent** in the **Type** list to set the species' concentration to a constant value (the value in the c_0 edit field). The Reaction Engineering Lab does not formulate a mass balance for the solvent species. The **Lock concentration/activity** check box is selected to underline that assumption. This setting corresponds to the situation where the solvent does not take part in chemical reactions at all, or where it reacts but is present in large excess. If you clear the **Lock concentration/activity** check box, the Reaction Engineering Lab sets up a material balance for the solvent species; the concentration takes on the initial value in the c_0 edit and is allowed to change with time.

Selecting a species to be at **Steady state** imposes the following condition on its material balance:

$$\frac{\partial c_i}{\partial t} = 0 . \quad (3-69)$$

This can be a useful assumption and simplification when reaction kinetic rates differ greatly, particularly in reactions that follow each other.

The General Page

Figure 3-14 shows the layout of the **General** page in the Species interface. The **Molecular weight** edit field, the **Thermo** tab, and the **Transport** tab are only available when you have selected the **Calculate thermodynamic properties** and the **Calculate species transport properties** check boxes. The **Feed Stream** tab is only available when you have selected one of the **Reactor types**; **Semibatch**, **CSTR** or **Plug-flow**. The above selections are made in the **Model Settings** dialog box (see Figure 3-4).

The **Parameters** area deals with species parameters. The first two edit fields are the species molecular weight, **M** (kg/mol) and the ionic charge, **z**. Values you enter for the molecular weight appear in the predefined expressions displayed in other edit fields. The following three edit fields include the critical temperature, **T_c** (K), the critical molar volume, **V_c** (m³/mol) and the critical compressibility factor, **Z_c**.

The **Density** edit field is active when you select a species as a solvent and when the **Calculate species transport properties** check box is selected in the **Model Settings** dialog box. The fluids density is compiled for both multicomponent and solute-solvent solutions. However, the **Density** edit field only displays the density of the solution for solvent-solute descriptions, when you select the solvent species in the **Species selection** list.

The ideal gas law is used to calculate the density of gases. The critical temperature, molar volume and compressibility factor are used to compute the density of liquid solvents. You can select **Gas** or **Liquid** as **Reacting fluid** in the **Model Settings** dialog box, see Figure 3-4.

For gas solvents, density, ρ , is expressed using the ideal gas law

$$\rho_{g,\text{solvent}} = \frac{p}{R_g T} M \quad (3-70)$$

where ρ_{solvent} denotes the solvent's density (kg/m^3), p the pressure (Pa), M the solvent's molecular weight (kg/mol), T the temperature (K), and R_g the ideal gas constant ($8.314 \text{ J}/(\text{mol}\cdot\text{K})$). Equation 3-70 uses the molar mass, **M**, for the solvent species, which you specify in the **Parameters** area of the **General** page.

For liquid solvents, the temperature-dependent density is given by the Rackett equation (Ref. 1)

$$\rho_{l,\text{solvent}} = \frac{M}{V_c Z_c \left(1 - \frac{T}{T_c}\right)^{\frac{2}{7}}} \quad (3-71)$$

where V_c denotes the critical molar volume (mol/m^3), Z_c the critical compressibility factor, and T_c the critical temperature (K) of the solvent species. Equation 3-71 uses the values you enter into the corresponding edit fields. Critical volumes, temperatures, and compressibility factors for a large number of species are readily available in engineering handbooks such as Ref. 2 and Ref. 3. Note that, if you do not intend to use the predefined expression from Equation 3-71 in your model, you do not need to supply the values for the critical constants.

The **Lock concentration/activity** check box removes the selected species' material balance, and the Reaction Engineering Lab also sets its concentration to the constant value in the **c₀** edit field. A locked species still affects the kinetics of appropriate reactions by appearing in the rate expressions as a constant. Note that you can use the **Lock activity/concentration** feature without having the species selected as solvent.

The solution of the material and energy balances require initial conditions for the reacting systems. Specify the initial concentrations in the **c₀** edit field. Note that these initial concentrations refer to species in the reactor volume of the Batch, Semibatch and CSTR reactors. For reactors with an inlet, that is the Semibatch and CSTR models, you also need to specify the species concentrations in the feed streams, **c_f**. When using the predefined Plug-flow reactor type, inlet molar flows, **F₀**, rather than initial

concentrations need to be supplied. Read more about specifying feed and inlet condition under the heading The Feed Streams Page on page 68.

Take special care when some species are involved in a reaction that is at chemical equilibrium. Under such conditions the equilibrium expression (Equation 3-55) introduces an algebraic relationship between the species' concentrations. In order to satisfy this relationship, one species' concentration must be directly linked to the concentration of the other. Dependent species are referred to as *slave species*. The Reaction Engineering Lab automatically selects the slave species, and the results appear in the **Mass Balance Parameters** dialog box. The number of slave species must be equal to the number of equilibrium reactions. Normally you do not need to change these settings.

Note: It is only possible to select slave species from the species that occur in equilibrium reactions.

You do not need to supply the initial concentrations for the slave species, because the Reaction Engineering Lab calculates their concentrations to satisfy the equilibrium expression (see section “Solver Parameters” on page 102). However, it is good practice to enter values into the **c₀** edit fields of slave species as well, as these values will be used as initial guesses to find slave species concentrations that are consistent with the equilibrium expressions.

The rate expression for a given species contains a contribution from each reaction in which the species participates so that

$$R_i = \sum_j \nu_{ij} r_j. \quad (3-72)$$

In Equation 3-72, r_j denotes the reaction rate (mol/(m³·s)) for reaction j , which is in turn given by Equation 3-49. ν_{ij} denotes the stoichiometric coefficient for species i in reaction j , defined as being negative for reactants and positive for products.

Note that you can modify or overwrite predefined expressions with arbitrary expressions of the modeled variables and the entities in other edit fields. Should you want to revert to the predefined expressions given for a specific species, select the species entry in the **Species selection** list and click the **Reset** button.

The Feed Stream Page

Figure 3-15 shows the layout of the **Feed Streams** page in the Species interface. The **Feed Stream** tab is only available when you have selected one of the **Reactor types**; **Semibatch**, **CSTR** or **Plug-flow**. The above selections are made in the **Model Settings** dialog box.

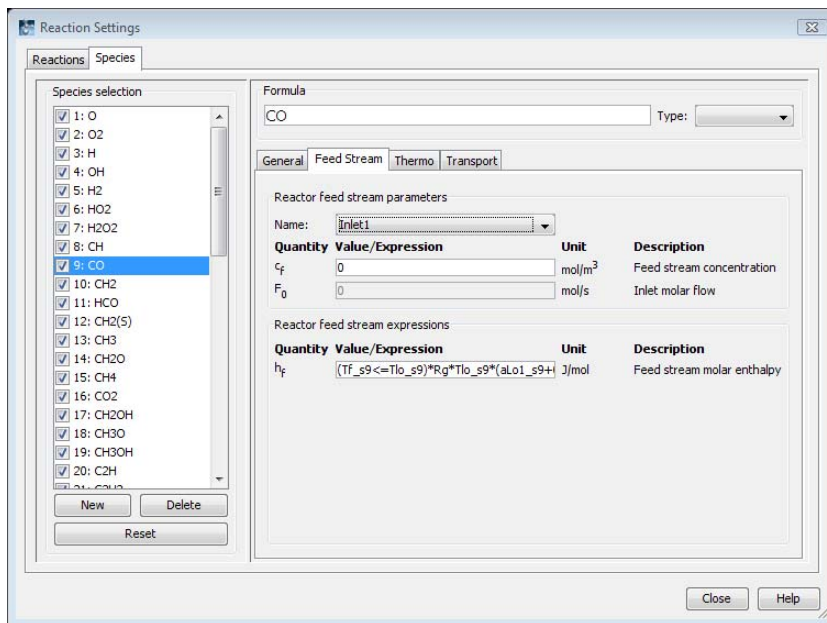


Figure 3-15: The Feed Stream page of the Species interface.

In the **Reactor feed stream parameters** area, you associate the species of the reacting fluid with the feed streams that supply them to the reactor volume. The **Name** list contains all feed streams defined in the **Model Settings>Feed Streams** dialog. To associate a species with a particular feed stream, first select the appropriate entry from the **Species selection** list and then select the feed stream from the **Name** list. Also, supply the concentration of the species in the feed stream by editing in the c_f field. The edit field F_0 corresponds to the species molar flow at the inlet of a plug-flow reactor. The edit field is available if the reactor type **Plug-flow** has been selected from the **Model Settings** dialog box.

The **Reactor feed stream expressions** area contains the **h_f** edit field. In this edit field you specify the species contribution to the molar enthalpy of the feed. For gases, the predefined expression in the **h_f** field is:

$$h_{f,i} = R_g \left(a_1 T_{f,i} + \frac{a_2}{2} T_{f,i}^2 + \frac{a_3}{3} T_{f,i}^3 + \frac{a_4}{4} T_{f,i}^4 + \frac{a_5}{5} T_{f,i}^5 + a_6 \right) \quad (3-73)$$

Note that Equation 3-73 is equivalent to thermodynamic polynomial expressed in Equation 3-75, evaluated at the feed stream temperature, $T_{f,i}$. The temperature of each feed stream is a reactor specific rather than a species-specific property, and you specify them in the **T_f** edit field found in the **Model Setting** dialog box. For liquids, no predefined expression is supplied in **h_f** edit field, and the default value is set to zero.

Read more of how Reaction Engineering Lab sets up and uses thermodynamic properties in the following section.

Figure 3-16 shows the layout of the **Thermo** page in the Species interface. The **Thermo** page is only available when you have selected the **Calculate thermodynamic properties** check box in the **Model Settings** dialog box.

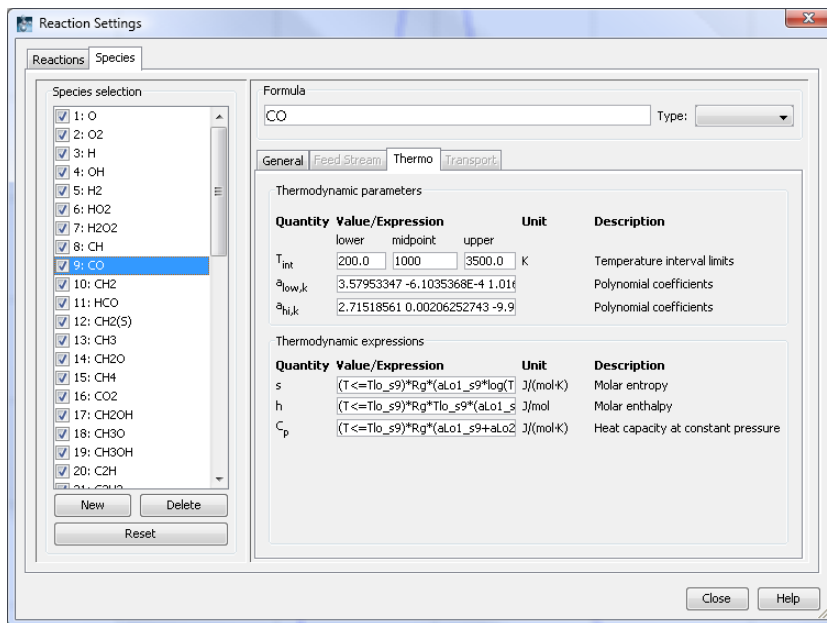


Figure 3-16: The Thermo page of the Species interface.

The top area of the **Thermo** page deals with **Thermodynamic parameters** and supplies inputs to fields in the **Thermodynamic expressions** area. Any coefficients for the thermodynamic polynomials (see below) you enter into the $a_{k,low}$ edit fields apply to the temperatures in the range $T_{int}/lower$ to $T_{int}/midpoint$; coefficients you enter into the $a_{k,high}$ edit fields apply to temperatures in the range $T_{int}/midpoint$ to $T_{int}/upper$ range.

At the bottom of the **Thermo** page you can see the **Thermodynamic expressions** area, which contains the edit field for the species' heat capacity, C_p , the molar enthalpy, h , and the molar entropy, s , using the polynomial format of Gordon and McBride (Ref. 5). This manual also refers to these expressions as NASA polynomials:

$$C_{p,i} = R_g(a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4) \quad (3-74)$$

$$h_i = R_g \left(a_1 T + \frac{a_2}{2} T^2 + \frac{a_3}{3} T^3 + \frac{a_4}{4} T^4 + \frac{a_5}{5} T^5 + a_6 \right) \quad (3-75)$$

$$s_i = R_g \left(a_1 \ln T + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7 \right) \quad (3-76)$$

Here, $C_{p,i}$ denotes the species' heat capacity (J/(mol·K)), T the temperature (K), and R_g the ideal gas constant, 8.314 (J/(mol·K)). Further, h_i is the species' molar enthalpy (J/mol), and s_i represents its molar entropy (J/(mol·K)), at standard state.

When you use the NASA polynomials as inputs to the Reaction Engineering Lab, enter the coefficients a_1 to a_7 directly into the corresponding edit fields. Then the predefined expressions given by Equation 3-74, Equation 3-75, and Equation 3-76 are ready to use. You can also import data files with the coefficients, as outlined in Importing Thermodynamics Files on page 129. Polynomial coefficients for NASA polynomials are available as public resources (Ref. 14).

WORKING WITH PREDEFINED EXPRESSIONS

The open and editable format of the Reaction Engineering Lab lets you choose whether to use the predefined expressions as given, use parts of a predefined format, or replace expressions entirely. A few short examples highlight the use of the predefined expressions used in the **Thermo** page to enter the thermodynamic properties of carbon monoxide. They also illustrate the possibilities to adapt to different modeling situations.

- Case 1—Carbon monoxide is part of a reacting mixture. You want to do several things: make use of the predefined expressions of species C_p as an input to the heat capacity of the reacting mixture (Equation 3-138); use the predefined expression h for each species to calculate the heat of reaction (Equation 3-65); and use the predefined expression s for each species to calculate the entropy of reaction

(Equation 3-66) and subsequently the equilibrium constant of reaction (Equation 3-51).

To accomplish this, enter the seven coefficients of the NASA format, a_1 to a_7 , into the appropriate edit fields, or import a CHEMKIN thermo input file (see Importing Thermodynamics Files on page 129).

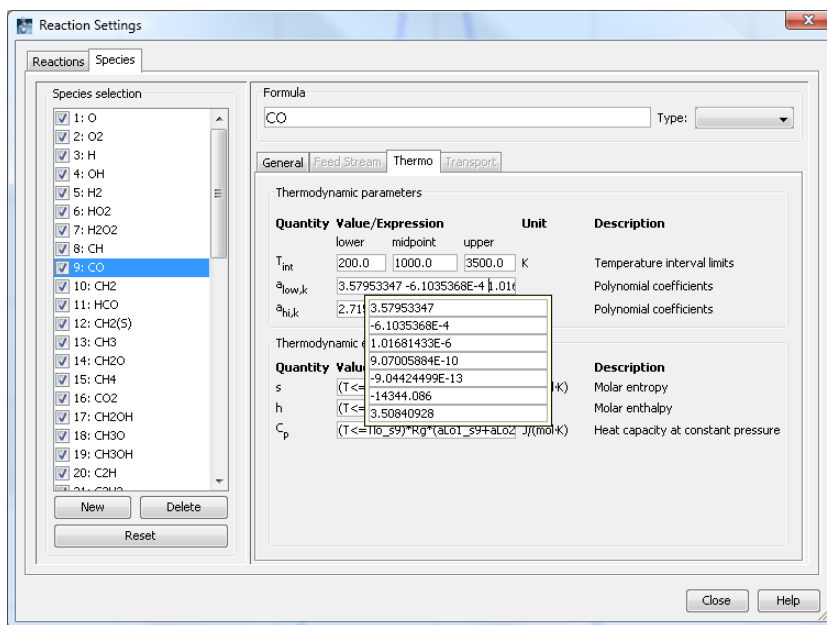


Figure 3-17: Enter the polynomial coefficients of the NASA format into the corresponding edit fields or import the data from file.

- Case 2—Carbon monoxide is part of a reacting mixture. You want to make use of the predefined expressions of species C_p to calculate the heat capacity of the reacting mixture (Equation 3-138).

Polynomials for C_p are available in the literature (Ref. 2, Ref. 3, and Ref. 4) in the frequently used form

$$C_p = R_g \sum_n a_n T^{n-1} \quad n = 1, \dots, 5 \quad (3-77)$$

You can directly use the predefined expression for the species' heat capacity, Equation 3-74, also given in the $\mathbf{C_p}$ edit field, by supplying coefficients in the $\mathbf{a_1}$ to $\mathbf{a_5}$ edit fields. Note that you can enter fewer than five coefficients.

You also want to use the predefined expressions h for each species to calculate the heat of reaction (Equation 3-65). An option is to make use of the heat of formation at standard state (298.15 K) to calculate the coefficient a_6 . Identifying the coefficient a_6 of Equation 3-75 is straightforward. In the NASA polynomial format, the species molar enthalpy is related to its heat capacity according to

$$h = \int_0^T C_p dT + h(0) \quad (3-78)$$

Inserting Equation 3-74 into Equation 3-78 and comparing the result with Equation 3-75 shows that the term $a_6 R_g$ is identified as the species enthalpy of formation at 0 K, that is, $h(0)$. Evaluate $h(0)$ from the species enthalpy of formation at standard state temperature, $T_{\text{std}} = 298.15$ K, which is given by

$$a_6 = \frac{h(T_{\text{std}})}{R_g} - \left(a_1 T_{\text{std}} + \frac{a_2}{2} T_{\text{std}}^2 + \frac{a_3}{3} T_{\text{std}}^3 + \frac{a_4}{4} T_{\text{std}}^4 + \frac{a_5}{5} T_{\text{std}}^5 \right). \quad (3-79)$$

Reaction Settings

Reactions | **Species**

Species selection

- ☒ 1: O
- ☒ 2: O2
- ☒ 3: H
- ☒ 4: OH
- ☒ 5: H2
- ☒ 6: H2O
- ☒ 7: H2O2
- ☒ 8: CH
- ☒ **9: CO**
- ☒ 10: CH2
- ☒ 11: HCO
- ☒ 12: CH2(S)
- ☒ 13: CH3
- ☒ 14: CH2O
- ☒ 15: CH4
- ☒ 16: CO2
- ☒ 17: CH2OH
- ☒ 18: CH3O
- ☒ 19: CH3OH
- ☒ 20: C2H

New Delete

Reset

Formula: CO Type: [dropdown]

General | **Feed Stream** | Thermo | Transport

Thermodynamic parameters

Quantity	Value/Expression	Unit	Description
T _{int}	lower: 200.0, midpoint: 1000.0, upper: 3500.0	K	Temperature interval limits
a _{low,k}	3.912 -3.913e-3 1.182e-5 -1.302		Polynomial coefficients
a _{hi,k}	2.71 3.912 -3.913e-3 1.182e-5 -1.302e-8		Polynomial coefficients
Thermodynamic			
s	(T<=298.15) 0.515e-11 (T<=298.15) 0	J/(mol·K)	Molar entropy
h	(T<=298.15) -1.4344e4 (T<=298.15) 0	J/(mol·K)	Molar enthalpy
C _p	(T<=110.59)*K*(a01_59+a02_59)/(mol·K)	J/(mol·K)	Heat capacity at constant pressure

Close Help

Figure 3-18: Enter the polynomial coefficients for C_p (a_1 to a_5) and coefficient a_6 evaluated from the enthalpy of formation at standard state.

- Case 3—Carbon monoxide is again part of a reacting mixture. It is satisfactory to approximate C_p as being constant. Specify the species enthalpy by making use of the heat of formation at 298 K, $h(298)$, according to the well-known expression

$$h = C_p(T - 298) + h(298) \quad (3-80)$$

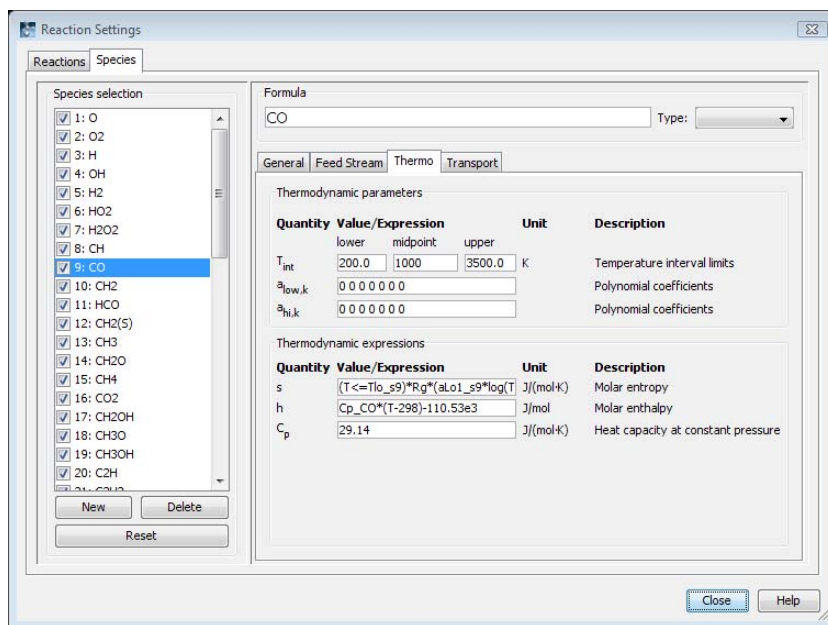


Figure 3-19: The predefined expression for C_p overwritten by a constant value, and the predefined expression for h overwritten by a user-defined expression.

Figure 3-20 shows the layout of the **Transport** page in the Species interface. The **Transport** page is only available when you have selected the **Calculate species transport properties** check box in the **Model Settings** dialog box.

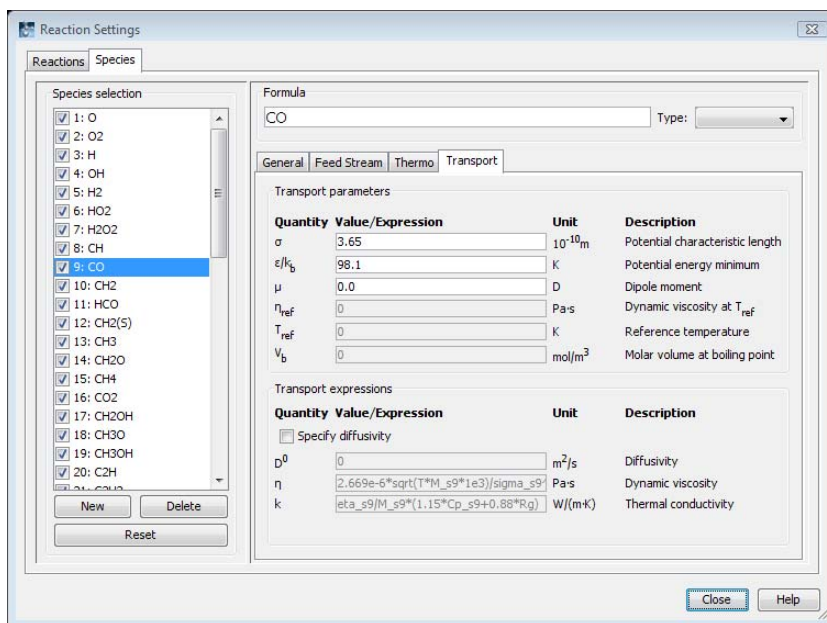


Figure 3-20: The Transport page in the Species interface.

At the top of the **Transport** page is the **Transport parameters** area, which supplies inputs to the expressions in the **Transport expressions** area. The first three parameters apply to gases: σ , the characteristic length (\AA) of the Lennard-Jones/Stockmayer potential; ϵ/k_b , the energy minimum (K) of the Lennard-Jones/Stockmayer potential; and μ , the dipole moment (Debye). The three parameters at the bottom of the area apply to liquids: η_{ref} is the liquid viscosity (Ns/m^2) of a species given at the temperature T_{ref} (K), while V_b is the molar volume at the boiling point (m^3/mol).

The bottom area of the **Transport** page, labeled **Expressions**, contains the edit field for the diffusivity, D^0 , the dynamic viscosity, η , and the thermal conductivity, k .

The Reaction Engineering Lab sets up different expressions for diffusivities depending on whether species are diffusing in a solvent or in a multicomponent mixture.

The most general description of a solution is the one that describes the solution as a multicomponent solution, where all species in a solution interact with each other. A simplified description, but still a common one, assumes that the solution consists of a solvent that dominates the properties of the solution. The solutes in such a solution interact only with solvent molecules.

For gases, the Reaction Engineering Lab calculates diffusion coefficients from the following expression based on kinetic gas theory:

$$D_{AB} = 2.695 \cdot 10^{-3} \cdot \frac{\sqrt{T^3(M_A + M_B)/(2 \cdot 10^3 M_A M_B)}}{p \sigma_A \sigma_B \Omega_D} \quad (3-81)$$

Here, D_{AB} is the binary diffusion coefficient (m^2/s), M equals the molecular weight (kg/mol), T represents the temperature (K), p is the pressure (Pa), and σ equals the characteristic length (\AA) of the Lennard-Jones/Stockmayer potential. In addition, Ω_D is the collision integral, given by the following equation (Ref. 7 and Ref. 8):

$$\begin{aligned} \Omega_D = & A(T^*)^{-B} + C[\exp(-DT^*)] + E[\exp(-FT^*)] \\ & + G[\exp(-HT^*)] + \frac{0.19\delta_{AB}^2}{T^*} \end{aligned} \quad (3-82)$$

where

$$T^* = k \frac{T}{\epsilon_{AB}} \quad (3-83)$$

$$\epsilon_{AB} = (\epsilon_A \epsilon_B)^{1/2} \quad (3-84)$$

$$\delta_{AB} = (\delta_A \delta_B)^{1/2} \quad (3-85)$$

$$\sigma_{AB} = (\sigma_A \sigma_B)^{1/2} \quad (3-86)$$

$$\delta = \frac{1}{2} \frac{\mu^2}{\epsilon \sigma^3} \quad (3-87)$$

In Equation 3-87, μ is the species dipole moment (Debye). For gases at moderate pressure, the binary diffusivity can be used for the multicomponent Maxwell-Stefan diffusivities.

To export the Maxwell-Stefan diffusivities from the Reaction Engineering Lab to COMSOL Multiphysics, selecting the export to the Maxwell-Stefan Diffusion and Convection Application mode. The Reaction Engineering Lab creates one diffusivity expression for each pair of species in the solution, so for multicomponent solutions the **Diffusivity** edit field is unavailable (there is generally not a single value). You find the expressions for the diffusivities in the **Export to COMSOL Multiphysics** dialog box and in the Maxwell-Stefan diffusivity matrix in the Maxwell-Stefan Diffusion and Convection application mode in the Chemical Engineering Module.

If a solvent approximation is used for gases, the binary diffusivities are used to calculate the diffusivity of species *A* in a solvent *B*. The expression of each species diffusivity in the solvent is then displayed in the **Diffusivity** edit field in the Reaction Engineering Lab.

For liquids, the diffusivity of a species *A* in a solvent *B* is calculated by the Reaction Engineering Lab using the Wilke-Chang equation (Ref. 9):

$$D_{AB} = 3.7 \cdot 10^{-15} \frac{(\phi_B M_B)^{1/2} T}{\eta_B V_{b,A}^{0.6}} \quad (3-88)$$

where η_B denotes the solvent's dynamic viscosity (Ns/m²), and $V_{b,A}$ equals the molar volume at the normal boiling point of the solute species (m³/mol). ϕ_B is the dimensionless association factor of the solvent, by default set to 1. The expression of each species diffusivity in the solvent is then displayed in the **Diffusivity** edit field in the Reaction Engineering Lab. Note that this requires that you select one of the species in the **Species selection** list as **Solvent**. The **Molar volume at boiling point** edit field is then only available for the solute species while the **Dynamic viscosity** and the **Reference temperature** edit fields are only available for the solvent species.

As mentioned already in the **General** page section above, the default settings implements a multicomponent solution consisting of all species in the **Species selection** list. This choice is appropriate when exporting to the Maxwell-Stefan Convection and Diffusion application mode in the Chemical Engineering Module. The solvent-solute approximation is appropriate for export to the Diffusion and Convection and Diffusion application modes in the Chemical Engineering Module.

Referring again to the **Transport** page on the Species interface of the **Reaction Settings** dialog box, the **Transport expressions** area displays expressions for the dynamic viscosity of the species. For gases, the predefined expression for the dynamic viscosity is given by the kinetic gas theory (Ref. 7 and Ref. 8) as

$$\eta_i = 2.669 \cdot 10^{-6} \frac{\sqrt{T(M_i \cdot 10^3)}}{\sigma_i^2 \Omega_v}. \quad (3-89)$$

Here η represents the dynamic viscosity (Ns/m²), and Ω_v is the collision integral, given by

$$\Omega_v = A(T^*)^{-B} + C[\exp(-DT^*)] + E[\exp(-FT^*)] + \frac{0.20\delta^2}{T^*} \quad (3-90)$$

with

$$T^* = k \frac{T}{\epsilon} \quad (3-91)$$

$$\delta = \frac{1}{2} \frac{\mu^2}{\epsilon \sigma^3} \quad (3-92)$$

In Equation 3-92, μ is the species dipole moment (Debye).

For liquids, an approximate expression for the temperature dependence of the dynamic viscosity is given by this equation (Ref. 10):

$$\eta = 10^{-3} \left((\eta_{\text{ref}} 10^3)^{-0.2661} + \frac{T - T_{\text{ref}}}{223} \right)^{-3.758} \quad (3-93)$$

where the dynamic viscosity η is given in Ns/m². As inputs for Equation 3-93, the Reaction Engineering Lab takes the reference viscosity, η_{ref} (N·s/m²) at the reference temperature T_{ref} (K), found in the **Transport parameters** area.

Finally, the **Transport expressions** area displays expressions for the species' thermal conductivity.

For gases, the predefined expression for thermal conductivity comes from the Stiel-Thodos equation (Ref. 11)

$$k = \frac{\eta}{M} (1.15 C_p + 0.88 R_g) \quad (3-94)$$

where the thermal conductivity k is in (W/(m·K)). Here C_p denotes the heat capacity (J/(mol·K)). Note that Equation 3-94 is a function of viscosity as given by Equation 3-89 and of the specific heat as given by Equation 3-74.

The Reaction Engineering Lab does not provide predefined expressions for the thermal conductivity of liquids. For liquids, you can type an arbitrary expression of composition, temperature or any other modeled entity, in the **k** edit field to calculate the thermal conductivity of liquid mixtures in order to use such an expression in the export to the Chemical Engineering Module.

Constants and Expressions

Choose **Model>Constants** to open the dialog box in Figure 3-21.

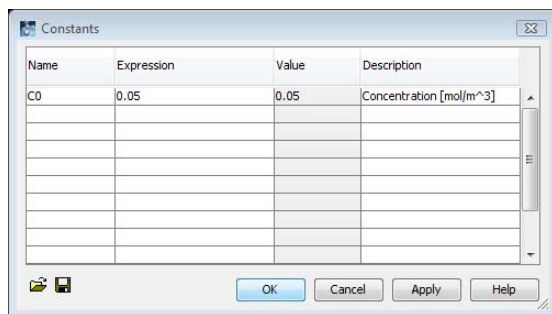


Figure 3-21: The Constants dialog box.

The Reaction Engineering Lab evaluates constants when you click **Apply** or **OK** in the **Constants** dialog box. Constants can depend on other constants and can contain any mathematical functions except dependent variables and the time variable from the model. You can use the **Constants** box to create your own temporary constants database. You can use constants in any expressions or edit field in the Reaction Engineering Lab.

To add a constant, type its designation in the **Name** edit field, then enter the expression that defines its value in the **Expression** edit field. This expression can use any constants already defined. Click **Apply** or click in another edit field to evaluate the constant. You can add optional text in the **Description** edit field.

It is possible to save constant lists to a text file as well as load constants from a text file into the **Constants** dialog box. To save your constants to a file, click the **Export Variables to File** button in the lower-left corner of the dialog box. The Reaction Engineering Lab saves the information in three tab-separated columns you define in the **Export Variables** dialog box. In each row, the first column contains the constant's name; the second column contains the expression that defines its value; and the third column contains an optional description.

You can also load constants from a text file where each row contains a constant's name, expression, and description separated by tabs or colons. To load such a file, click the **Import Variables from File** button in the lower-left corner of the **Constants** dialog box. This opens the **Import Variables** dialog box, where you can browse for text files. The

Reaction Engineering Lab adds the constants to the end of the current list in the dialog box.

Now move on to the **Model>Expressions** dialog box in Figure 3-22.

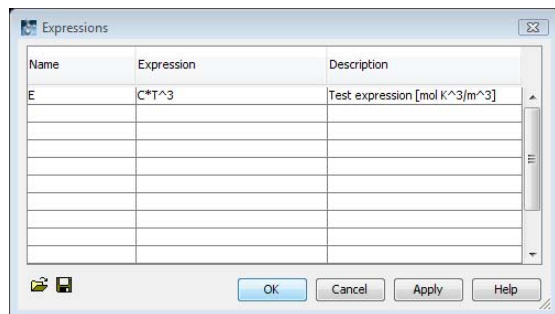


Figure 3-22: The Expressions dialog box.

Expression variables can make a model easier to understand by introducing short names for complicated expressions. Another use for expression variables is during postprocessing.

To add an expression, type an appropriate entry in the **Name** edit field, then in the **Expression** field enter the relationship that defines the variable. These expressions can include arbitrary functions of the dependent variables (concentrations and temperature) and the time variable in your model as well as the constants defined in the **Constants** dialog box. You can also add optional text to identify the variable in the **Description** edit field. You can save expressions to text files and also load such expressions from text files into the **Expressions** dialog box.

Solver Parameters

Figure 3-23 shows the contents of the **Simulation>Solver Parameters** dialog box.

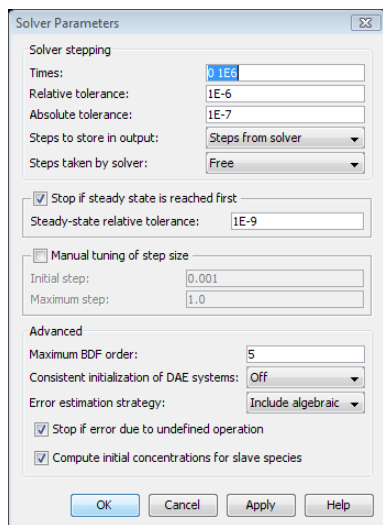


Figure 3-23: The Solver Parameters dialog box.

The default setting for the Reaction Engineering Lab solver is to run the simulation until the system reaches steady state, within the specified time frame in the **Times** edit field. This is done by calculating a norm for the time derivatives of the species concentrations and once this norm is small enough, compared to the tolerance that you set in the **Steady-state relative tolerance** edit field, the solution process stops. If steady state is not reached within the specified time frame, the solver stops at the maximum time. The default relative tolerance for the steady-state condition is 10^{-9} . The solver stops when the following expression becomes negative:

$$t^2 \sum_i \left(\frac{dc_i}{dt} \right)^2 - \text{rtol}^2 \sum_i c_i^2$$

You can also actively enter a solution time in the **Time stepping** area if you know the time span of the process. The **Times** edit field contains a vector of times in seconds for which the Reaction Engineering Lab calculates the solution. The default vector is 0 1e6, which represents times from 0 to 10^6 s. If you want to make sure that the solver

computes the solution for the entire time span, clear the **Stop if steady state is reached first** check box. Note also that you need to clear the **Stop if steady state is reached first** when solving models using the Semibatch and CSTR reactor types, where the initial concentration of reactants is zero.

The absolute and relative tolerances control the error in each integration step during the time-stepping process. For one dependent variable (solution component), the relative error is, roughly stated, less than the relative tolerance if the value of the dependent variable is large, and the absolute error is less than the absolute tolerance if the value of the dependent variable is small. The **Relative tolerance** edit field only accepts a positive number as input (default = $1\text{e-}6$). The **Absolute tolerance** edit field accepts two different entries. You can set the **Absolute tolerance** to a positive number (default = $1\text{e-}7$) or you can specify it as a space-separated list whose entries alternate between the name of a dependent variable and a positive scalar. For example, entering a sequence like `c_a 1e-7 c_b 1e-5` makes it possible to set different absolute tolerances for different species, in this case for species *a* and *b*.

The Reaction Engineering Lab uses the solver's internal steps as default for postprocessing results, so these time steps are normally independent of the intermediate times you specify in the **Times** edit field. To obtain solution results at the times in the **Times** edit field rather than the solution at the times chosen by the solver, go to the **Times to store output** list and select **Specified times**.

To control how the solver takes its internal time steps, select the appropriate options in the **Time steps taken by solver** list. For the **Free** selection, the solver steps are controlled by the step length controller, in order to satisfy the tolerance for the simulation. If you select **Strict**, the solver must take a time step at each of the values in the **Times** edit field, and it also adds times in between as necessary. The **Strict** selection is useful when an equation involves transient steps or irregularities that the time stepping must not skip. Adding times around each such event ensures that the solver resolves them. For the **Intermediate** selection, the solver must take at least one time step in the intervals defined with the list in the **Times** edit field.

Selecting the **Manual tuning of step size** check box just below the **Time stepping** area makes it possible to set the initial internal time step and the upper limit of the internal time steps.

In the **Advanced** area you control additional settings of the time-stepping algorithm. The **Maximum BDF order** edit field (BDF = *backward differentiation formula*) accepts an integer between 1 and 5 that sets the degree of the interpolating polynomial used

in the time-stepping method. A smaller value results in a more stable numerical scheme at the expense of an increased number of time steps.

Models set up in the Reaction Engineering Lab are often *differential-algebraic* problems. A system of differential-algebraic equations (DAEs) has constraints imposed on the initial values, for instance, that an algebraic equation must be satisfied (such as the equilibrium relation).

By default the Reaction Engineering Lab makes an initialization of slave species concentrations for models that contain equilibrium reactions. For these models, the initial concentrations of slave species are computed from the initial concentrations of the other (non-slave) species and the equilibrium relations before solving the time-dependent problem. The initial concentrations entered for each slave species are used as a starting guess when finding the consistent initial concentrations. It may sometimes be necessary to change the initial guesses in order to find valid initial concentrations. After computing the initial concentrations, the Reaction Engineering Lab solves the DAE system over time. Use the **Compute initial concentrations for slave species** check box to manually disable the slave species initialization procedure.

The above procedure ensures that the initial values are consistent for DAE systems formed by equilibrium reactions. Other model properties can also result in a DAE system, for example, if some species are set to steady state. For such systems the DAE solver can perturb the initial values so that they become consistent with the imposed constraints. The selection in the **Consistent initialization of DAE systems** list controls how the solver perturbs initial values. Select **Backward Euler** for index-1 and index-2 DAEs. The solver then perturbs the initial values of all degrees of freedom (DOFs) by taking a backward Euler step, giving a small perturbation to the differential DOFs. Select **On** for index-1 DAEs. The solver then fixes the values of the differential DOFs (to those given by the initial value) and then solves for the initial values of the algebraic DOFs and the time derivative of the differential DOFs. When applicable, this selection is preferable to **Backward Euler** because it does not perturb the values of the differential DOFs. The default setting is **Off**, which indicates that the initial values are already consistent and that the solver does not need to modify them. This setting is recommended for pure ODE systems and DAE systems initialized by computing the consistent slave species initial concentrations.

For DAE systems, the selection **Exclude algebraic** in the **Error estimation strategy** list excludes the algebraic DOFs from the error norm.

By default, the solver stops with an error message when it encounters an undefined mathematical operation in an expression that appears in the model settings, for

instance, division by zero or square root of a negative number. To change this behavior, clear the **Stop if error due to undefined operation** check box. Then the solver treats the result of the operation as **Inf** (infinity) or **NaN** (not a number). This feature can be useful in a nonlinear problem where the steps in the iterative solution process lead to variable values for which an expression is undefined. The solver then reduces the step size in the Newton iteration when it encounters **Inf** or **NaN** so that it can find a solution.

The Reaction Engineering Lab uses a dedicated version of the DAE solver DASPK, developed by Dr. Linda Petzold of the University of California, Santa Barbara (Ref. 12).

Parameter Estimation Settings

In order to use a reaction model to perform system analysis and design, you need to know the relevant kinetic parameters. When not available, the parameters can be found by properly adjusting the theoretical model so that simulated results match experimental data. This process is referred to as parameter estimation.

Typical applications of parameter estimation involves evaluating:

- Rate constants for isothermal systems
- Arrhenius parameters for non-isothermal systems
- Reaction order
- Estimating non-kinetic parameters

You can readily solve such problems within the graphical user interface of the Reaction Engineering Lab. When doing so, the work flow often involves the following steps:

- Formulating a reaction model by entering the chemical reactions and selecting a reactor type
- Reading experimental data into the graphical user interface
- Associating measured variables with the variables of the reaction model
- Selecting parameters and performing estimation by minimizing the objective least-squares function
- Evaluating the ability of the model to represent the experimental data

You find hands-on examples illustrating how to solve parameter estimation problems in the section “Model Validation and Calibration” on page 29, as well as more extensive examples the Model library.

To set up a parameter estimation problem, select the menu item **Estimation>Parameter Estimation Settings** or click the **Parameter Estimation Settings** button on the Main toolbar.

The Data Page

The **Data** page provides an overview of the experimental data that has been loaded into Reaction Engineering Lab. To import data in the form of text files, click the **Import From File** button. You can also import data structures set up in COMSOL Script by clicking the **Import From Workspace** button. Equivalently, you can load data into the

user interface by choosing **File>Import>Experimental Data From File** or **File>Import>Experimental Data From Workspace**. These two options are described in detail in “Importing Experimental Data” on page 135.

You are free to load multiple data into the software. You may further choose to include one or more data sets into the parameter estimation calculations.

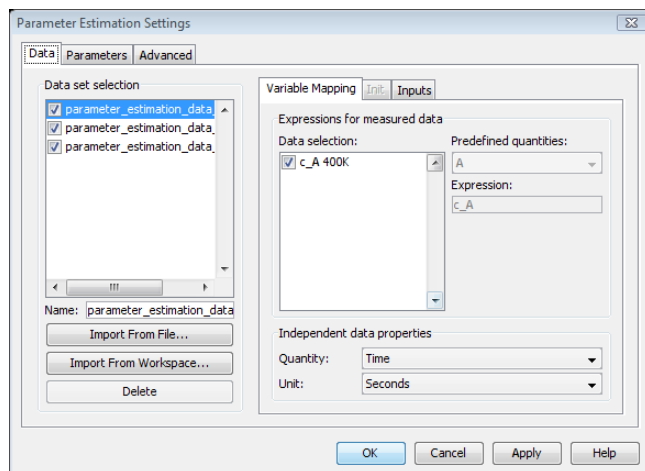


Figure 3-24: The Parameter Estimation Settings dialog box displaying the Data page.

The names of loaded data sets appear in the **Data set selection** list. Click the **Delete** button to remove selected data sets from the list. You can also deactivate a data set by clearing the associated check box.

The **Data** page contains the following subpages:

- **Variable Mapping**
- **Init**
- **Inputs**

THE VARIABLE MAPPING PAGE

On the **Variable Mapping** page, the **Data selection** list displays the names of the columns containing the dependent variables of the measured data. Columns of data can be deactivated by clearing the check box to the left of the list entry. You can associate the measured variables with the reaction model variables by choosing the appropriate entry in the **Data selection** list and then selecting corresponding variable name from the **Predefined quantities** list, as illustrated in Figure 3-24. If a batch reactor type is being

modeled, the list contains the concentration variables defined in the **Reaction Settings** dialog. If you are using a plug-flow reactor type, the **Predefined quantities** list contains the species molar flow variables. You can also associate measured and model variables by entering a user-defined expression in the **Expression** edit field.

At the bottom of the **Variable Mapping** page, you find the **Independent data properties** area. The independent variable of the experimental data set is assumed to be in the first column of the data file. For instance, this could be a list of times at which measurements have been performed. From the **Quantity** list you can select Time, Residence time or Volume, whichever is appropriate to represent the independent variable of the measured data. The appropriate unit of the data is selected from the **Unit** list. Time given in Seconds is the default selection for the batch reactor types and reactor Volume in Cubic meters is default for the plug-flow reactor type.

THE INIT PAGE

You use the **Init** page when you want the software to account for multiple data sets in the parameter estimation calculations, where the initial concentrations of reacting species vary among the sets. When parameters other than initial concentrations change with data set, then use the **Inputs** page, as outlined in the following section.

The **Init** page is deactivated by default. You activate the page by selecting the **Advanced** setting **Specify initial state values for data sets**.

Note that if you perform parameter estimation using data sets that specify varying initial species concentrations, then initial concentrations are assumed to be known quantities and cannot be selected as parameters to be estimated.

THE INPUTS PAGE

You use the **Inputs** page when parameters other than initial concentrations have different values for different data sets. The page contains a list where you can specify parameters that vary from set to set. The values of these parameters are known, and come to affect the evaluation of the reaction model. Examples of input parameters are

the temperature, amount of catalyst, and so on. The parameter names in the list are identical to the names of constants or expressions defined in the reaction model.

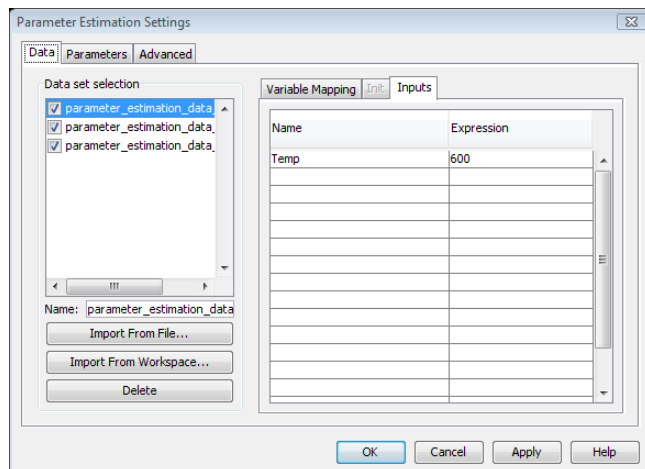


Figure 3-25: Working with multiple data sets you specify known parameters that vary from set to set on the Inputs page.

The Parameters Page

On the **Parameters** page you select the parameters that you want to estimate. Depending on reaction model selections, the **Predefined parameters** list displays a number of default parameters, such as rate constants, Arrhenius parameters, and initial concentrations. You can move over to the **Parameters to estimate** list by selecting entries from the **Predefined parameters** and then clicking the **Add** button (>) or the **Add all** button (>>). You can also specify user-defined parameter names in the **Expression**

edit field, and add them (>). Remove entries from the **Parameters to estimate** list by clicking the **Remove (<)** or **Remove all (<<)** buttons.

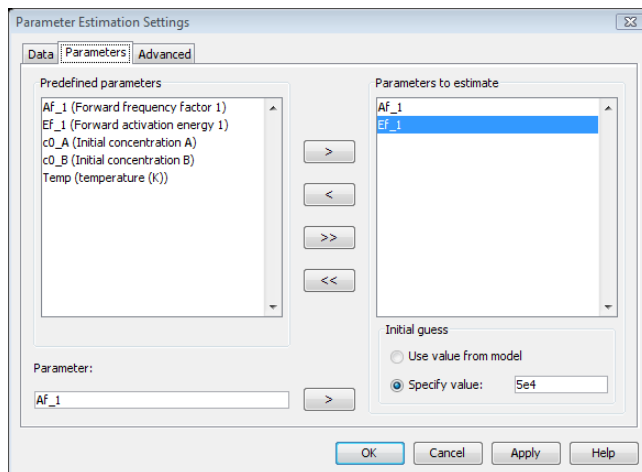


Figure 3-26: Specify the parameters to be included in the parameter estimation calculation.

In the **Initial guess** area, you specify an initial guess for each of the parameter values that you are about to estimate. By default, the **Use value from model** radio button is selected. This causes the software to use the current value of the parameter specified in the reaction model. For example, if you want to evaluate the frequency factor and activation energy of an irreversible reaction, the values in the **Frequency factor** and

Activation energy found in the **Reaction Settings** dialog box will be used as initial guesses.

Reaction Settings

Reactions Species

Reaction selection

1: A=>B

Formula

A=>B Type: Irreversible

Kinetics Thermo

☒ Use Arrhenius expressions

Arrhenius parameters

Quantity	Value/Expression	Unit	Description
A	50e3		Frequency factor
n	0		Temperature exponent
E	15e3	J/mol	Activation energy

Kinetic expressions

Quantity	Value/Expression	Unit	Description
k_f	$A \cdot T^n \cdot \exp(-E_f/(R \cdot T))$		Forward rate constant
k_r	0		Reverse rate constant
<input type="checkbox"/> Specify equilibrium constant			
k_{eq_0}	0		Equilibrium constant
k_{eq}	0		Equilibrium expression
r	$k_f \cdot c_A$	mol/(m ³ ·s)	Reaction rate

New Delete Reset

Close Help

Figure 3-27: Initial guesses for parameter estimation calculations can be taken directly from the reaction model.

As an alternative you can select the **Specify value** and type the initial guess into the associated edit field.

The Advanced Page

Advanced page contains settings for the non-linear least squares (NLS) algorithm, used for parameter estimation. The settings and default values are:

- Maximum number of iterations in search direction; 50
- Maximum number of iterations in the line search; 50
- Tolerance for the gradient; 1e-6
- Minimum relative decrease in the cost function; 1e-6
- Lower bound for the singular values of the Jacobian; 1e-6
- Confidence level; 0.95

The value set in the **Confidence level** edit field determines the confidence interval calculated by the software. The default value is 0.95, which indicates that a 95% confidence interval is evaluated using the standard normal distribution. Once a parameter estimation calculation has been performed, the upper and lower limits of the confidence interval are displayed in the **Log - Progress** window.

Additional settings control how the software handles initial data sets. By default, the **Specify initial state values for data sets** check box is cleared. When this setting is cleared and multiple data sets are included in a parameter estimation calculation, it is assumed that parameters varying from set to set do not include initial concentrations. Known parameters changing with data set are provide on the Inputs page. When **Specify initial state values for data sets** check box is selected, you can use multiple data sets where initial concentrations change from set to set. The values are entered on the Init page.

Selecting **Copy parameter values to model after parameter estimation** automatically updates the reaction model with the estimated parameters values. You find the calibrated values where the parameters were originally defined. Typically this would be in the Reaction Settings dialog box or in the Constants dialog box.

The **Solve model after estimating parameters** check box is selected by default, and is only available if the **Copy parameter values to model after parameter estimation** is also selected. As indicated, the selection automatically solves the reaction model immediately after the parameter estimation calculation is completed.

The Log Page

Solving a reaction model or performing a parameter estimation calculation opens the **Progress** window. You can also access this window by selecting either of the menu items **Simulation>View Log** or **Estimation>View Log**. On the **Log** page you can see the progress of simulation as well as parameter estimation.

The parameter estimation log summarizes the steps of the NLS algorithm, listing the loss function and stop conditions. Furthermore, a summary report is generated listing the calculated values of estimated parameters, the standard error and the upper and lower limits of the confidence interval.

Algorithm for Parameter Estimation

For parameter estimation calculations, Reaction Engineering Lab uses a non-linear least squares (NLS) algorithm implementing the Gauss-Newton method.

PROBLEM DEFINITION AND NOTATION

A general problem formulation is to estimate the parameter in the model:

$$y = H(x_0, \theta, u, e, v) \quad (3-95)$$

In Equation 3-95, x_0 denotes the known or unknown initial state vector. θ contains the unknown parameters in the model, u is a known input signal, e is a stochastic measurement noise, and v is an unknown stochastic input signal.

The general solution can be stated as minimizing the sum of least squares

$$V(\eta) = \frac{1}{2} \sum_{t=1}^N \varepsilon^T(t_k, \eta) \varepsilon(t_k, \eta) \quad (3-96)$$

The parameter vector η does not have to include all parameters and initial states, but rather a subset of them.

$$\eta = (x_0^T, \theta^T)^T \quad (3-97)$$

The residual ε is defined component-wise as

$$\varepsilon(t_k, \eta) = y(t_k) - \hat{y}(t_k, \eta) \quad (3-98)$$

Equation 3-96 is also known as the loss function.

ALGORITHM

The Newton-Raphson method for NLS can be stated as iterating

$$\eta^{i+1} = \eta^i - \mu \left(\frac{\partial^2 V(\eta^i)}{\partial \eta^2} \right)^{-1} \frac{\partial}{\partial \eta} V(\eta^i) \quad (3-99)$$

until convergence. The Jacobian and Hessian in Equation 3-99 are given by

$$\frac{\partial}{\partial \eta} V(\eta) = \sum_{k=1}^N \frac{\partial}{\partial \eta} \varepsilon^T(t_k, \eta) \varepsilon(t_k, \eta) = J(\eta) \varepsilon(\eta) \quad (3-100)$$

and

$$\frac{\partial^2 V(\eta)}{\partial \eta \partial \eta^T} = J(\eta)J^T(\eta) - \frac{\partial}{\partial \eta} J(\eta) \varepsilon(\eta) \quad (3-101)$$

The Gauss-Newton method approximates the Newton-Raphson method with the assumption that the second term of the Hessian is an order of magnitude smaller than the first term, so that

$$\frac{\partial^2 V(\eta)}{\partial \eta \partial \eta^T} \approx J(\eta)J^T(\eta) \quad (3-102)$$

The Gauss-Newton method for NLS can thus be stated as iterating

$$\eta^{i+1} = \eta^i - \mu^j (J(\eta^i)J^T(\eta^i))^{-1} J(\eta^i) \varepsilon(\eta^i) \quad (3-103)$$

where μ is the step size. The gradient J is evaluated numerically.

PARAMETER ESTIMATION FUNCTIONS

The parameter estimation functionality available through the Reaction Engineering Lab graphical user interface is also available in COMSOL Script. Type `help reaction` at the Script prompt to learn more about structure and functionality of the parameter estimation function and objects.

Plot Parameters

Select the menu item **Postprocessing>Plot Parameters** or the **Plot Parameters** button to bring up the dialog box in Figure 3-28.

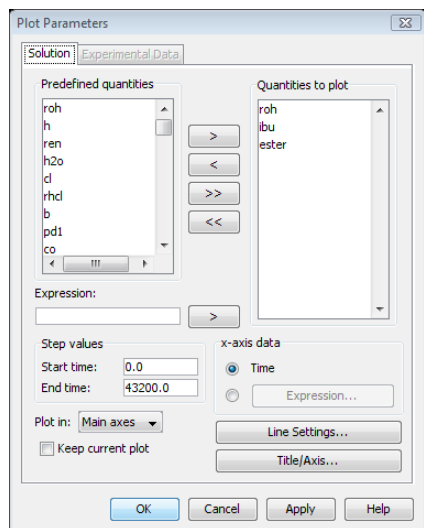


Figure 3-28: The Plot Parameters dialog box.

The Solution page

The **Predefined quantities** list shows variables set up after the solution of a given reaction model. By default, it lists the variables for all species' concentrations, the temperature, the reaction rates, the rate expressions per species, and any variable name you have entered in the **Expressions** list.

The **Quantities to plot** list shows the variables designated for plotting. When the Reaction Engineering Lab solves a reaction model for the first time, it plots all species' concentrations in the main user-interface window. To add variables from the **Predefined quantities** list to the **Quantities to plot** list, click the Add button, **>**, or the Add All button, **>>**. Remove variables from the **Quantities to plot** list by clicking the Remove button, **<**, or the Remove All button, **<<**. To add more expressions to the **Quantities to plot** list, type them into the **Expression** edit field just below the **Predefined quantities** list and then click the Add button **>**. Entries can be arbitrary constants or expressions as well as predefined variables in the Reaction Engineering Lab.

The **Start time** and **End time** edit fields let you select a specific time interval in which to plot entries in the **Quantities to plot** list. The zoom tools update this time interval when you use them to change the plot.

Click the **Line Settings** button to bring up the corresponding dialog box. Select the desired line color, line style, or line marker settings for the respective plot variables. The default settings create solid lines with colors that cycle. Select the **Legend** check box to include a legend of the traces in the plot window. Select the **Show labels on lines** check box to add labels with the names of the plotted quantities on the respective lines.

Back in the **Plot Parameters** dialog box, click the **Title/Axis** button to bring up the **Title/Axis Settings** dialog box. To overwrite the default axis titles, clear the **Auto** check box and type the desired text into the **x label** and **y label** edit fields. Select the **Log scale** check box to change an axis scale from linear to logarithmic.

Selections in the **Plot in** list let you plot the simulation results in the **Main axes** of the primary user-interface window, in a **New figure** window, or in an existing figure window when applicable. To plot different groups from the **Quantities to plot** list on top of one another, select the **Keep current plot** check box. To plot experimental data points on top of an existing plot, select the **Plot experimental data** check box. This last check box is available only if you have already read external data into the user interface with the menu selection **File>Import>Experimental Data**. Further information on how to import data into the Reaction Engineering Lab appears in the following section.

The Experimental Data Page

The **Data sets to plot** list shows the file names of all data sets currently loaded into the software. The check box immediately to the left of the data set name allows you to activate the or deactivate the plotting of the indicated data set.

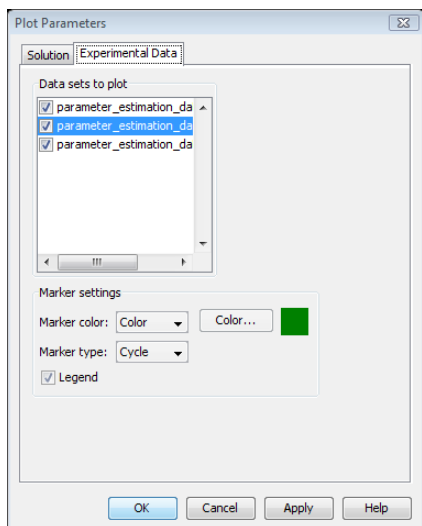


Figure 3-29: Control the plotting of data sets from the Experimental Data page.

The **Marker settings** of each data set can be changed with respect to **Marker color** and **Marker type**. You can also select to show the **Legend** associated with each set.

Zooming Into the Plots

To zoom into an interesting section of the plot, use the **Zoom Horizontal** toolbar button. It provides an easy way to select a start time and end time for the plot. Until you start a new model, the Reaction Engineering Lab keeps the selected time span unless you click the **Zoom Extents** button to get the full time span (or use any of the other zoom tools).

Importing CHEMKIN Files

The Reaction Engineering Lab can import CHEMKIN files to simulate complex chemical reactions in the gas phase (Ref. 13). These input files contain three basic sets of information:

- Chemical kinetics
- Species thermodynamic properties
- Species transport properties

The Reaction Engineering Lab can use the imported data to:

- Set up and solve mass and energy balances for ideal reactor systems (batch reactors, semi-batch reactors, CSTRs, and plug-flow reactors)
- Set up and evaluate species transport properties as a function of reactor conditions
- Set up and mass, energy, and momentum balances for space-dependent models, and export them to COMSOL Multiphysics

It is possible to read the input files for kinetics, thermodynamic, and transport properties independently and use them as separate data resources. For instance, if you have entered a set of reactions into the Reaction Engineering Lab's graphical user interface, you can supply species thermodynamic and transport data by reading the appropriate input files. The full functionality of the Reaction Engineering Lab is retained even after the import procedure. This means that all expressions and all data imported into the software are available for reference and for editing in the GUI.

Data files describing reaction kinetics, species thermodynamics, and species transport properties are published on the World Wide Web and are readily available (Ref. 14).

Importing Kinetics Files

The Reaction Engineering Lab can import and interpret the data contained in CHEMKIN input files describing gas-phase kinetics.

To import a kinetics file, select the menu item **File>Import>CHEMKIN Kinetics Input File**. Reading a kinetics file is equivalent to creating a new reaction model, and you are therefore prompted to save the model to the file you are currently working with. When the **Import CHEMKIN Kinetics Input File** dialog box opens up, browse to the desired file and click the **Import** button. To view the imported set of reactions, click the **Reaction Settings** button on the Main toolbar.

UNITS

The Reaction Engineering Lab interprets unit keywords contained in kinetics input files and automatically performs a conversion to SI units upon import.

SYMBOLS AND SPECIES LABELING

The notation used for different reaction types in both the Reaction Engineering Lab and CHEMKIN input overlap to a large degree:

SYMBOL	REACTION ENGINEERING LAB	CHEMKIN INPUT
=>	irreversible	irreversible
<=>	reversible	reversible
=	equilibrium	reversible

Note, though, that the Reaction Engineering Lab interprets the = delimiter in a CHEMKIN input file as a marker for a reversible reaction, replacing the delimiter with <=> in the graphical user interface. In the Reaction Engineering Lab, the = delimiter is reserved for reactions of the equilibrium type (see the section The Kinetics Page on page 75).

The Reaction Engineering Lab can read any species labels used in a kinetics input file. Once the file has been imported, the chemical species, as indicated by their respective label, are displayed in the **Reaction Settings** dialog box in the **Reaction selection** and **Species selection** lists.

To make the representation of expressions and variable names as compact as possible, the Reaction Engineering Lab automatically assigns associated species labels based on their position in the **Species selection** list. For the position i in the **Species selection** list,

the assigned name is simply *si* (*species i*). The species variable and parameter names are in turn indexed with this label.

Figure 3-30 illustrates automatic species and parameter naming. Here H2O2 is the species name imported from the CHEMKIN input file. When the reactions are imported, the Reaction Engineering Lab automatically creates the **Species selection** list, in this case with H2O2 placed in position 7. The associated species name is subsequently set to *s7*, with parameters and variables using this label as an index. When you position the cursor over an edit field's name, the corresponding variable name is displayed as a tooltip. In the figure, the H2O2 has the variable name **M_s7** assigned to the molecular weight.

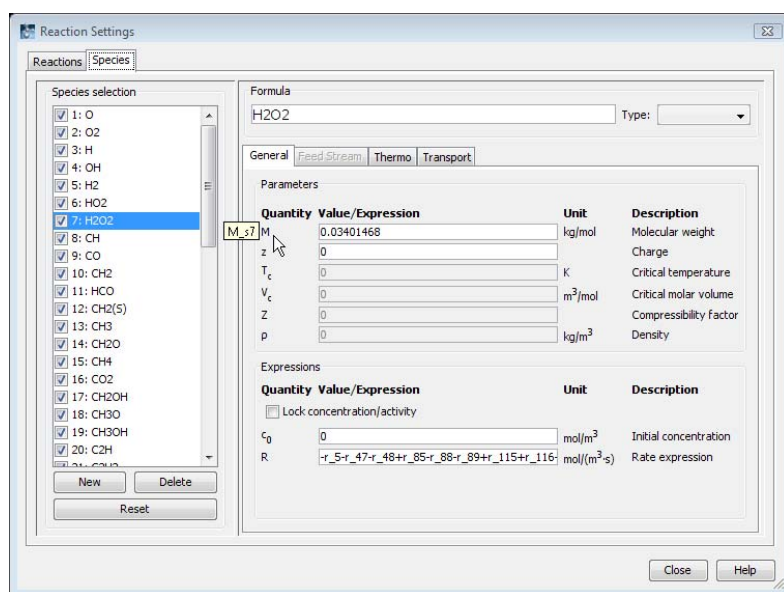
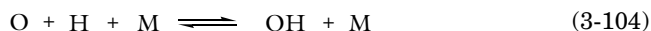
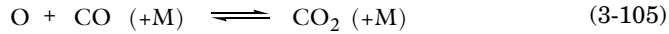


Figure 3-30: The position in the Species selection list is used to create a species label that appears in parameters and variable names.

The species labels *M* and *(+M)* that occur in kinetics files have special significance. *M* refers to a third body species that takes part in a reaction without being consumed:



The presence of *(+M)* in a reaction indicates that the effect of the third body is pressure dependent:



As an example, the reaction between oxygen and carbon monoxide occurs in the absence of a third body at high pressures, while at low pressures a third body is required for the reaction to proceed.

The third body represents all species in the reaction mixture. As a consequence, there is no separate M species generated in the **Species selection** list. The effect of the third body is rather seen on rates of the reactions where M is present (see Kinetics Expressions in the following section).

Kinetic Expressions

Both the Reaction Engineering Lab and a CHEMKIN kinetics input make use of the mass-action law to specify the rate of a generic chemical reaction ($\text{mol}/(\text{m}^3 \cdot \text{s})$):

$$r_j = k_j^f \prod_{i \in \text{react}} c_i^{-\nu_{ij}} - k_j^r \prod_{i \in \text{prod}} c_i^{\nu_{ij}}. \quad (3-106)$$

Here, k_j^f and k_j^r denote the forward and reverse rate constants, respectively, c_i is the concentration of species i (mol/m^3), and ν_{ij} are stoichiometric coefficients. ν_{ij} are defined as being negative for reactants and positive for products.

By default, a CHEMKIN input specifies the forward rate constant by supplying the corresponding Arrhenius parameters A_j^f , n_j^f , and E_j^f to the equation

$$k_j^f = A_j^f T^{n_j^f} \exp\left(-\frac{E_j^f}{R_g T}\right). \quad (3-107)$$

The standard way to calculate the reverse rate constant is using the relationship

$$k_j^r = \frac{k_j^f}{K_{0,j}^{\text{eq}}}. \quad (3-108)$$

In this equation, $K_{0,j}^{\text{eq}}$ is the equilibrium constant expressed in concentration units (mol/m^3). The equilibrium constant given in pressure units (atm) can be evaluated from the NASA thermodynamic polynomials (Ref. X):

$$K_{p,j}^{\text{eq}} = \exp\left(\frac{S_i}{R_g} - \frac{H_i}{R_g T}\right) \quad (3-109)$$

$$K_{0,j}^{\text{eq}} = K_{p,j}^{\text{eq}} \left(\frac{p_0}{R_g T} \right)^{\sum_i \nu_{ij}}. \quad (3-110)$$

The thermodynamic polynomials required to evaluate Equation 3-107 are predefined in the Reaction Engineering Lab, and the requisite coefficients are imported from a thermodynamics file (see the section Importing Thermodynamics Files on page 129).

The kinetics expressions just given can be identified directly in the Reaction Engineering Lab user interface. As illustrated in Figure 3-31, you find Equation 3-106 represented in the **Reaction rate** edit field, Equation 3-107 in the **Forward rate constant** edit field, Equation 3-108 in the **Reverse rate constant** edit field, and Equation 3-110 in the **Equilibrium constant** edit field.

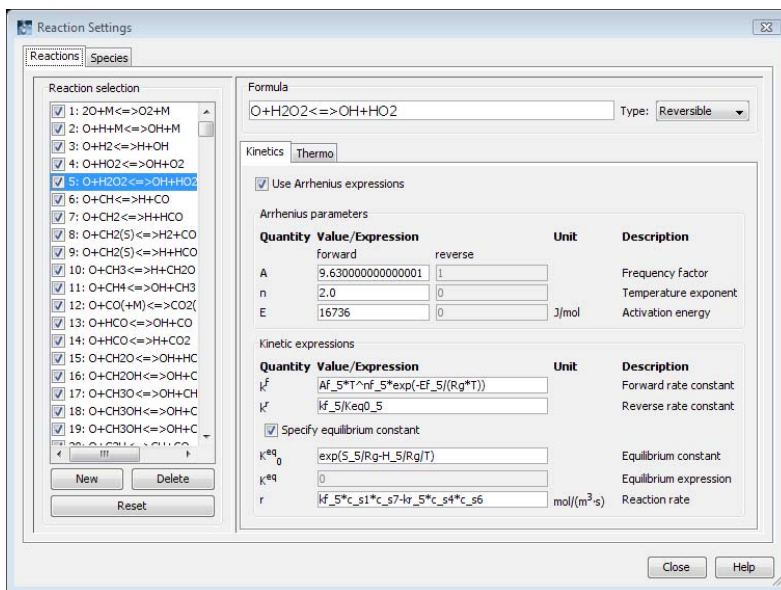


Figure 3-31: All kinetics parameters and rate expressions are presented in the Reactions interface of the Reaction Settings dialog box.

THIRD BODY REACTIONS

A reaction containing the species M indicates that a third body takes part in the reaction without being consumed in the process (see, for example, Equation 3-104). The third body species represents all species present in the reacting mixture, leading to the following expression for the reaction rate:

$$r_j = c_{\text{eff}} \left(k_j^f \prod_{i \in \text{react}} c_i^{-\nu_{ij}} - k_j^r \prod_{i \in \text{prod}} c_i^{\nu_{ij}} \right) \quad (3-111)$$

where

$$c_{\text{eff}} = \left(\sum_i b_{ij} c_i \right) \quad (3-112)$$

The second factor on the right-hand side of Equation 3-111 is the default reaction rate (Equation 3-106). The factor c_{eff} corresponds to the total concentration of the reacting gas. The parameter b_{ij} is the species efficiency factor, taking into account that certain species act more efficiently as third bodies. Expressions taking the form of Equation 3-112 are automatically set up in the **Reaction rate** edit field if a third body reaction is imported from a file.

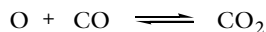
PRESSURE-DEPENDENT THIRD BODY REACTIONS

A reaction containing the species (+M) indicates a pressure-dependent third body reaction.

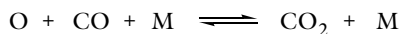
In a first class of pressure-dependent kinetics, a reaction occurs in the absence of a third body at high pressures, while a third body is required for the reaction to proceed at low pressures (unimolecular/recombination fall-off reactions). A reaction of this class is indicated by the **LOW** keyword in a CHEMKIN kinetics file (see the section Supported Keywords on page 126).

Consider an example:

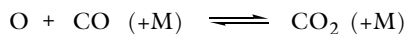
At high pressure, oxygen and carbon monoxide react directly:



At low pressure, a third species promotes the reaction:



In the Reaction Engineering Lab and in the kinetics input files, the two reactions are summarized using the symbol (+M):



Separate Arrhenius parameters are required for both the high-pressure region,

$$k_{\infty} = A_{\infty} T^{n_{\infty}} \exp\left(-\frac{E_{\infty}}{R_g T}\right) \quad (3-113)$$

and the low-pressure region,

$$k_0 = A_0 T^{n_0} \exp\left(-\frac{E_0}{R_g T}\right) . \quad (3-114)$$

The rate constant at any pressure is given by

$$k = k_{\infty} \left(\frac{P_r}{1 + P_r} \right) F \quad (3-115)$$

where the reduced pressure is expressed as

$$P_r = \frac{k_0 c_{\text{eff}}}{k_{\infty}} . \quad (3-116)$$

The Arrhenius parameters for the high-pressure region are imported into the **Reactions/Kinetics** page in the **Frequency factor**, **Temperature exponent**, and **Activation energy** edit fields. The Arrhenius parameters for the low-pressure region are directly used to set up an expression equivalent to Equation 3-114. The complete expression

for the rate constant (Equation 3-115) is presented in the **Forward rate constant** edit field.

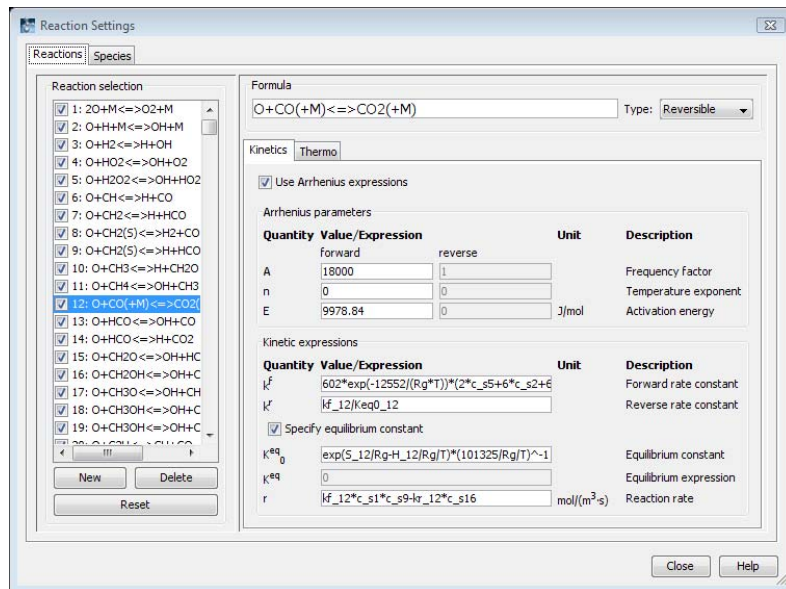


Figure 3-32: The full expression for a pressure-dependent rate constant is presented in the Forward rate constant edit field.

The expression for F in Equation 3-115 can have three different forms describing the blending of k_∞ and k_0 . The selection of the blending function, F , is indicated in kinetics files by the appropriate keyword along with the requisite set of function parameters. The Reaction Engineering Lab supports the following descriptions of F :

- Lindemann (Ref. 15):

$$F = 1 \quad (3-117)$$

- Troe (Ref. 16):

$$\log F = \left[1 + \left(\frac{\log P_r + c}{n - d(\log P_r + c)} \right)^2 \right]^{-1} \log F_{\text{cent}} \quad (3-118)$$

where

$$c = -0.4 - 0.67 \log F_{\text{cent}} \quad (3-119)$$

$$n = 0.75 - 1.27 \log F_{\text{cent}} \quad (3-120)$$

$$d = 0.14 \quad (3-121)$$

$$F_{\text{cent}} = (1 - \alpha) \exp\left(\frac{-T}{T^{***}}\right) + \alpha \exp\left(\frac{-T}{T^*}\right) + \exp\left(\frac{-T^{**}}{T}\right) \quad (3-122)$$

- SRI (Ref. 17):

$$F = d \left[a \exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right) \right]^X T^e \quad (3-123)$$

$$X = \frac{1}{1 + (\log P_r)^2}. \quad (3-124)$$

In a second class of pressure-dependent kinetics, a reaction occurs in the absence of a third body at low pressures, while a third body is required for the reaction to proceed at high pressures (chemically activated bimolecular reactions). A reaction of this class is indicated with the **HIGH** keyword in a kinetics file (see the section Supported Keywords on page 126).

Pressure-dependent rate constants are set up in a similar fashion as just explained. Separate Arrhenius coefficients are provided for the high- and low-pressure limits with the transition between the two regimes being described by the same blending functions F . The Arrhenius parameters for the low-pressure region are imported into on the **Reactions/Kinetics** page in the **Frequency factor**, **Temperature exponent**, and **Activation energy** edit fields, and the complete expression for the rate constant appears in the **Forward rate constant** edit field.

Supported Keywords

CHEMKIN kinetics files can include auxiliary reaction data that serve to modify the the standard format of kinetic expressions. Auxiliary reaction data is indicated in the input file with specific keywords. The Reaction Engineering Lab supports the following keywords:

- REV
- FORD
- RORD
- DUPLICATE
- LOW

- HIGH
- TROE
- SRI

SPECIFIED REVERSE REACTIONS

The REV keyword in a kinetics input file signals that the Arrhenius parameters are specified for the reverse rate constant in addition to the parameters for the forward reaction. In such a case, the Reaction Engineering Lab imports these parameters into the corresponding edit field (A_j^r , n_j^r , and E_j^r) and provides an expression in the Arrhenius form in the **Reverse rate** constant edit field:

$$k_j^r = A_r T^{n_r} \exp\left(-\frac{E_r}{R_g T}\right) \quad (3-125)$$

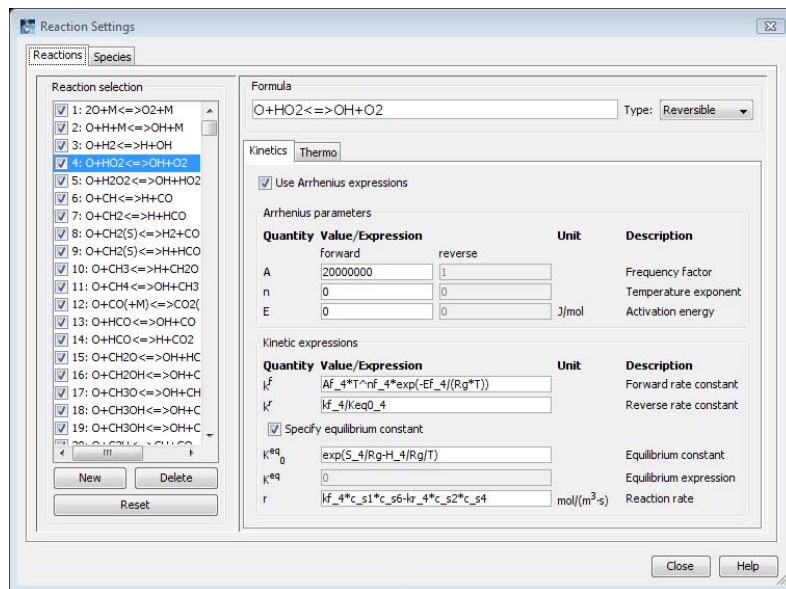


Figure 3-33: When importing a kinetics file containing the REV keyword, the Reaction Engineering Lab describes the reverse rate constant using an Arrhenius expression.

SPECIFIED REACTION ORDER

The FORD and RORD keywords indicate that the reaction rate does not follow the mass-action law, that is, the reaction order with respect to a species is different than the

absolute value of the stoichiometric coefficient of that species in the specified reaction. In the kinetics input file, each occurrence of the **FORD** or **FORD** keyword is followed by a species name and a number that indicates the new reaction order. The Reaction Engineering Lab adjusts for the new reaction order directly in the reaction rate expression, which it displays in the **r** edit field.

DUPLICATE REACTIONS

The keyword **DUPLICATE** (**DUP**) is used in kinetics files for each identical occurrence of a reaction formula. This feature accounts for the fact that two or more reactions have the same reaction mechanism but different rate parameters. The Reaction Engineering Lab can import any number of identical reaction formulas.

PRESSURE DEPENDENT REACTIONS

In a kinetics input file, the **LOW** keyword signals a reaction that is pressure dependent at low pressures (unimolecular/recombination fall-off reactions). The Arrhenius coefficients on the reaction line are for the high-pressure limit, while the Arrhenius parameters on the auxiliary information line are for the low-pressure limit.

In contrast, the **HIGH** keyword indicates a reaction that is pressure dependent at high pressures (bimolecular/recombination reactions). The Arrhenius coefficients on the reaction line are for the low-pressure limit, while the Arrhenius parameters on the auxiliary information line are for the high-pressure limit.

Additional keywords specify the form of the blending function, F . A Troe pressure dependence is set up if the **LOW** or **HIGH** keyword is followed by the **TROE** keyword along with three or four parameters (a , T^{***} , T^* , and T^{**}). A SRI pressure dependence is set up if the **LOW** or **HIGH** keyword is followed by the **SRI** keyword together with three or five parameters (a , b , c , d , and e). If no additional keyword follows **LOW** or **HIGH**, then a Lindemann pressure dependence is assumed. For further reading on the blending function F , see the section Kinetic Expressions on page 121.

Importing Thermodynamics Files

The Reaction Engineering Lab can import and properly interpret the data contained in CHEMKIN input files describing the thermodynamic properties of gas-phase species.

To import a kinetics file, select the menu item **File>Import>CHEMKIN Thermo Input File**. When the **Import CHEMKIN Thermo Input File** dialog box opens up, browse to the desired file and click the **Import** button.

The amount of data that the Reaction Engineering Lab imports from a thermodynamics file depends on the number of entries in the **Species selection** list. If the list is empty, it imports all the data from the thermo file and creates the corresponding new species entries. If the **Species selection** list already has entries, the Reaction Engineering Lab uses the species labels to identify entries in the thermodynamics file, and it then imports only the corresponding species data.

Because the Reaction Engineering Lab can read thermodynamics files separately without the prior import of a kinetics file, the files can be used as data resources for user-defined chemistries.

A CHEMKIN thermodynamic input file contains mainly sets of coefficients used to set up thermodynamic polynomials in the format of Gordon and McBride (Ref. 5). These polynomials describe the species heat capacity (J/(mol·K)), enthalpy (J/mol), and entropy (J/(mol·K)), at standard state:

$$C_{p,i} = R_g(a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4) \quad (3-126)$$

$$h_i = R_g\left(a_1T + \frac{a_2}{2}T^2 + \frac{a_3}{3}T^3 + \frac{a_4}{4}T^4 + \frac{a_5}{5}T^5 + a_6\right) \quad (3-127)$$

$$s_i = R_g\left(a_1\ln T + a_2T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7\right) \quad (3-128)$$

Each species in the thermo file is associated with seven polynomial coefficients ($a_1 - a_7$) for two temperature intervals. Once you have imported the file into the Reaction Engineering Lab, the thermodynamic coefficients for the respective temperature interval appear on the **Thermo** page that appears on the **Species** interface. Furthermore, Equation 3-126 appears in the **Heat capacity** edit field, Equation 3-127 in the **Molar enthalpy** edit field, and Equation 3-128 in the **Molar entropy** edit field.

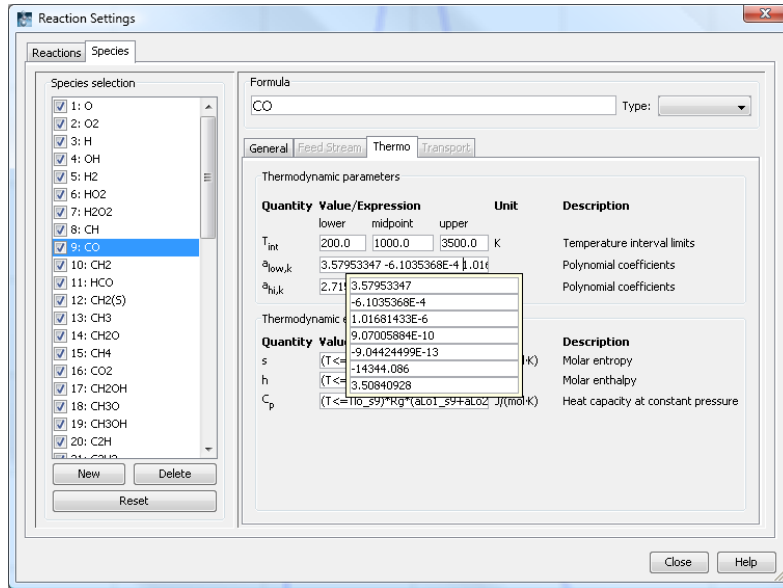


Figure 3-34: The NASA thermodynamic polynomials and the associated coefficients appear on the Thermo page in the Species interface.

From the species thermodynamic data and the stoichiometry, the Reaction Engineering Lab automatically sets up the related thermodynamics for chemical reactions, that is, the enthalpy of reaction (J/mol)

$$H_j = \sum_i v_{ij} h_i \quad (3-129)$$

the entropy of reaction (J/(mol·K))

$$S_j = \sum_i v_{ij} s_i \quad (3-130)$$

and the heat source of reaction (J/(m³·s))

$$Q_j = -H_j r_j \quad (3-131)$$

It presents these expressions on the **Thermo** page of the **Reactions** interface.

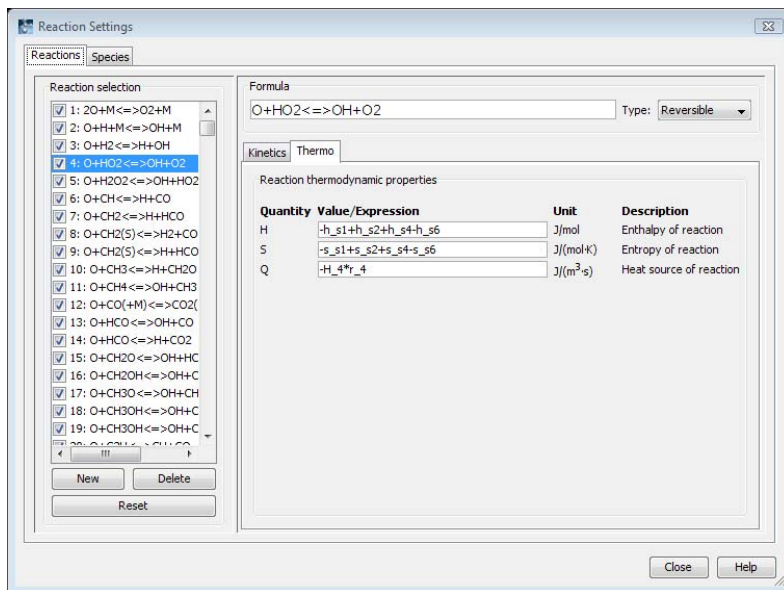


Figure 3-35: The reaction thermodynamic expressions appear on the Thermo page in the Reactions interface.

As noted previously, the reaction thermodynamic expressions can, in turn, be used to describe the equilibrium constant. The Gibbs free energy of reaction is

$$G_j = H_j - TS_j \quad (3-132)$$

and hence

$$K_{p,j}^{\text{eq}} = \exp\left(-\frac{G_j}{R_g T}\right) = \exp\left(\frac{S_j}{R_g} - \frac{H_j}{R_g T}\right) \quad (3-133)$$

A thermodynamics input file also contains information about the atomic composition associated with a given species label. Upon importing a file, the Reaction Engineering Lab uses this information to calculate the species molecular weight (kg/mol), which appears in the **Molecular weight** edit field on the **Species/General** page.

Some kinetics input files might be appended with the species thermodynamic data. In these instances, reading the kinetics files imports both kinetics and thermodynamic data into the Reaction Engineering Lab.

You can read more about the thermodynamic expressions defined in the Reaction Engineering Lab in the section The Thermo Page on page 89.

Importing Transport Files

The Reaction Engineering Lab can import and properly interpret the data contained in CHEMKIN input files describing the transport properties of gas-phase species.

To import a kinetics file, select the menu item **File>Import>CHEMKIN Transport Input File**. When the **Import CHEMKIN Transport Input File** dialog box opens up, browse to the desired file and click the **Import** button.

The amount of data that the Reaction Engineering Lab imports from the transport file depends on the number of entries in the **Species selection** list. If the list is empty, all data from the transport file is imported and the software creates the corresponding new species entries. If the **Species selection** list already has entries, the Reaction Engineering Lab uses the species labels to identify entries in the transport file, and it imports only the corresponding species data.

Because the Reaction Engineering Lab can read transport files separately without the prior import of a kinetics file, you can use these files as data resources for user-defined chemistries.

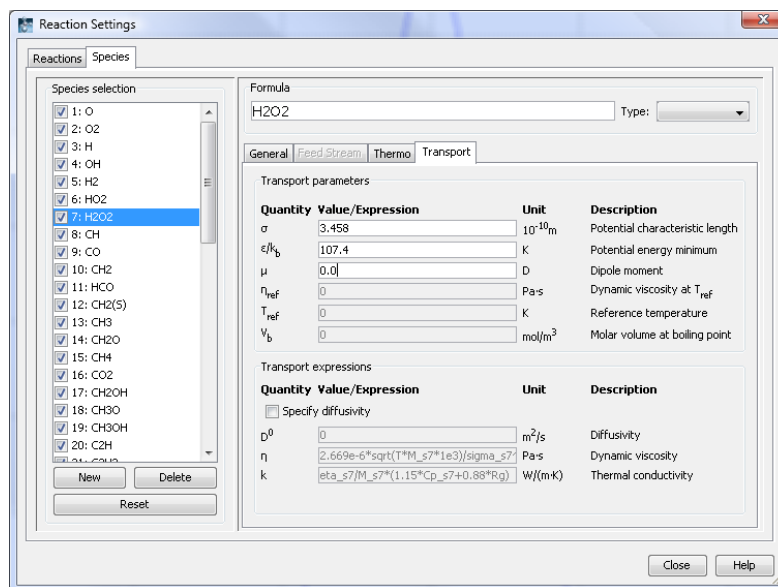


Figure 3-36: Species transport expressions along with the associated interaction potential parameters are given on the Transport page in the Species interface.

Each species in a transport file is associated with a data set of six parameters. From this file the Reaction Engineering Lab extracts the energy minimum of the Lennard-Jones potential well, ϵ/k_b (K), the Lennard-Jones characteristic collision length, σ (10^{-10} m), and the dipole moment of each species, μ (Debye). As illustrated in Figure 3-36, you find the imported values on the **Transport** page in the **Species** interface.

The Reaction Engineering Lab makes use of the imported parameters to set up expressions for a set of transport properties. Binary diffusion coefficients (m^2/s) are calculated according to

$$D_{AB} = 2.695 \cdot 10^{-3} \cdot \frac{\sqrt{T^3(M_A + M_B)/(2 \cdot 10^3 M_A M_B)}}{p \sigma_A \sigma_B \Omega_D} \quad (3-134)$$

The dynamic viscosity (Ns/m^2) is given by

$$\eta_i = 2.669 \cdot 10^{-6} \frac{\sqrt{T(M_i \cdot 10^3)}}{\sigma_i^2 \Omega_v} \quad (3-135)$$

and the thermal conductivity ($W/(m \cdot K)$) is expressed as

$$k = \frac{\eta}{M} (1.15 C_p + 0.88 R_g) \quad (3-136)$$

Predefined expressions corresponding to Equation 3-134, Equation 3-135, and Equation 3-136 are provided in the **Transport expressions** area of the **Transport** page.

You can read more about the thermodynamic expressions defined in the Reaction Engineering Lab in the section “The Transport Page” on page 95.

Importing Experimental Data

You can load experimental data to the Reaction Engineering Lab workspace in two different ways. The simplest way is to import data from a file, which you do by choosing **File>Import>Experimental Data From File**. The data file has to be organized in columns. The first column represents the sample time and the subsequent columns represent the samples concentrations or temperature. Elements in different columns can be separated by tabs or spaces. The first row in every column has to contain a string with the label of the corresponding measured entity. The contents of the string is used in the legend when plotting in the Reaction Engineering Lab. The following table shows an example of a data file on the required format for a system with species *A* and *B* measured at different times *t*:

't'	'c_A'	'c_B'
60	5.0	4.1
120	3.5	6.5
180	1.1	7.0
240	0	7.1
300	0	5.0

Once you have loaded the data into the Reaction Engineering Lab workspace, you can plot it by choosing **Postprocessing>Plot Parameters** and then selecting the **Plot experimental data** check box in the **Plot Parameters** dialog box.

The second way of loading experimental data to Reaction Engineering Lab is to import the data from the COMSOL Script workspace as a structure. You can do this by selecting **File>Import>Experimental Data from Workspace**. With this feature, you can use COMSOL Script to organize sets of external data points in a structure variable that the Reaction Engineering Lab can read. The data structure has a similar format as the data files: The first field is the vector *x*, typically containing times at which measurements have been performed. The second field is a matrix *y*, whose columns typically contain concentrations of a species measured at the times specified in *x*. The third field, **legend**, contains a cell array of strings of the same size as the number of columns in *y*; the string contents are displayed as trace legends when the Reaction Engineering Lab plots the data. Using the previous example, you then organize the structure as follows:

- 1 Create a column vector of the experimental time data:
`t=[60 120 180 240 300]'`
- 2 Create a matrix of the experimental concentration data, with each column vector corresponding to the concentrations of a given species:
`c=[[5 3.5 1.1 0 0]' [4.1 6.5 7 7.1 5]']`
- 3 Create a structure variable `expdata` and defined the x and y fields:
`expdata.x=t;`
`expdata.y=c;`
- 4 Add trace labels with the `legend` field:
`expdata.legend={'cA data', 'cB data'};`
- 5 In the Reaction Engineering Lab, select the menu item **File>Import>Experimental Data from Workspace**, then in the **Experimental data** dialog box enter `expdata`.
- 6 To plot the data, open the **Postprocessing>Plot Parameters** dialog box and select the **Plot experimental data** check box.

Exporting Reaction Models

The Reaction Engineering Lab sets up models for species that are reacting in ideal reactor systems. It describes material and energy balances with a system of ordinary differential equations (ODEs) that, when solved, shows the evolution of species concentrations and system temperatures over time or as a function of one space variable.

At times, you may want to perform an extended analysis of the reaction model, going beyond the functionality of the Reaction Engineering Lab. For instance, to study how a reacting system's detailed geometry impacts the concentration and temperature distributions, you can export a reaction model to COMSOL Multiphysics, where the space- and time-dependent model can be set up and solved. As another option, you export a reaction model to the COMSOL Script environment. In Script, you can for instance run parametric studies or perform advanced postprocessing. The following sections describe both of these options.

Export to Application Modes in the Chemical Engineering Module

An application mode in COMSOL Multiphysics is a predefined modeling interface describing a specific type of phenomenon. For instance, chemical engineering type problems typically involve mass, energy, and momentum transport, and you find the corresponding classes of application modes in COMSOL Multiphysics. You can export reaction models set up in the Reaction Engineering Lab to application modes of the Chemical Engineering Module, the MEMS Module, and the Earth Science Module. Expressions generated in the Reaction Engineering Lab, describing reaction kinetics, thermodynamics and transport properties, are inserted automatically into relevant edit fields of the application modes, thus greatly simplifying the modeling of reacting systems.

You can export your reaction models to one or more of the following application modes:

- Diffusion
- Convection and Diffusion
- Maxwell-Stefan Diffusion and Convection
- Nernst-Planck
- Electrokinetic Flow

- Solute Transport
- Conduction
- Convection and Conduction
- Conduction in Porous Media
- Convection and Conduction in Porous Media
- Incompressible Navier-Stokes
- Weakly Compressible Navier-Stokes
- General Laminar Flow

Once you have exported to COMSOL Multiphysics you can add any other application mode in to include effects of, for example, electric fields for electrochemical systems. You can do this for any model geometry in 1D, 1D axial symmetry, 2D, 2D axial symmetry, or 3D.

To export a reaction model to COMSOL Multiphysics, first go to the Main menu and select **File>Export>Model to COMSOL Multiphysics** or click the corresponding quick button on the Main toolbar. This will launch COMSOL Multiphysics if it is not already running. A dialog box prompts you for the space dimension of the transport model: 1D, 1D axial symmetry, 2D, 2D axial symmetry, or 3D (Figure 3-37).

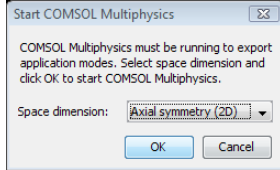


Figure 3-37: To export reaction models to COMSOL Multiphysics, that program must be running. It first prompts you for the space dimension of the multiphysics model.

After selecting a space dimension, the **Export to COMSOL Multiphysics** dialog box appears (Figure 3-38).

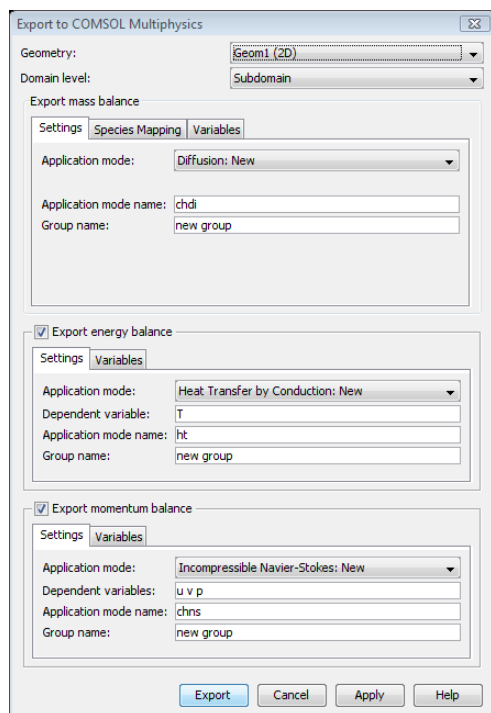


Figure 3-38: The Export to COMSOL Multiphysics dialog box contains selections for the export of reaction models to applicable application modes of the Chemical Engineering Module.

At the top of this dialog box, the **Geometry** list shows the geometries available in the current multiphysics model. Note that if you are creating a new multiphysics model, only one geometry, with the dimensions that you selected in the **Start COMSOL Multiphysics** dialog box, is available in the **Geometry** list.

You can include several geometries in a model if you want to model several coupled reacting systems to model, for example, cascade coupled reactors. The export of a given reaction model is always associated with a specific geometry, but you can run multiple exports from the Reaction Engineering Lab to set up a model with several geometries. This also allows you to define different reaction settings in different geometries in a model.

The **Domain level** list contains the choices **Subdomain**, **Boundary**, and **Interior Boundary**. Your selection determines if the application mode is exported to a subdomain group or a boundary group. The boundary conditions are different on interior boundaries than on the exterior boundaries. They therefore require a separate boundary group. For the exterior boundaries, select **Boundary** in the **Domain level** list. You can run multiple exports if you want to use different reaction sets in different subdomains or at different boundaries.

The **Export mass balance** area consists of the **Settings**, the **Species Mapping**, and the **Variables** pages. The **Settings** page contains the **Application mode** list with these choices:

- Diffusion
- Convection and Diffusion
- Nernst-Planck
- Electrokinetic Flow
- Maxwell-Stefan Diffusion and Convection
- Solute Transport

Selecting a new application mode, for example, **Diffusion:New** in the **Application mode** list, creates an application mode with the name you provide in the **Application mode name** edit field, and it associates exported groups with that mode. You can also select an already existing application mode from the **Application mode** list. Regardless of if you are selecting a new or existing application mode, you can enter any name in the **Group name** edit field. You can use different groups to simulate different kinetics models using the same application mode.

Click the **Species Mapping** tab to display the names of the species in the Reaction Engineering Model and the corresponding names of the dependent variables in the COMSOL Multiphysics application mode. To export a group to an existing application mode you can map the species concentration in the Reaction Engineering Lab model on the existing names for the species concentration in the active application mode running in COMSOL Multiphysics. For reaction models containing equilibrium reactions, the slave species selection must also be mapped to the corresponding slave concentration in the COMSOL Multiphysics application mode.

All mass balance application modes except Maxwell-Stefan Diffusion and Convection use the default variable names according to the syntax `c_speciesname`, referring to species concentrations in mole per volume. When exporting to the Maxwell-Stefan application mode, the default variable name follows the syntax `w_speciesname`, referring to the species weight fraction. The Reaction Engineering Lab automatically

calculates initial weight fractions of the reaction model from the initial concentrations and molecular weights you enter on the **Species>General** page.

An additional consideration of the Maxwell-Stefan Diffusion and Convection application mode is the order of the species in the **Species Mapping** page. For this application mode, the Reaction Engineering Lab eliminates the mass balance of the last species variable in the setup of the mass balance equations. You can rearrange the order of entries in the **Species Mapping** page by right-clicking on the name of the species in the **Species selection** list and then selecting **Move Up** or **Move Down**.

Click the **Variables** tab (the third tab in the **Export mass balance** area) to view a list of variables for export, which are not available elsewhere in the user interface. In general, these variables are not used for modeling in the Reaction Engineering Lab but are necessary for modeling in the Chemical Engineering Module. The listed expressions depend on the selection in the **Application mode** list. For instance, expressions for binary diffusion coefficients (Equation 3-81) appear when you choose the Maxwell-Stefan Diffusion and Convection application mode.

Now move on to the **Export energy balance** area, which consists of the **Settings** page and the **Variables** page. The **Settings** page contains the **Application mode** list, which contains the application modes:

- Conduction
- Convection and Conduction
- Conduction in Porous Media
- Convection and Conduction in Porous Media

The list of dependent variables is here seen in the **Settings** page, but otherwise the structure of the **Export energy balance** area is analogous to that of the **Export mass balance** area above. Expressions listed on the **Variables** page depend on your choice in the **Application mode** list. For reacting multicomponent mixtures, the following mixture properties are defined:

- density (kg/m³)

$$\rho_{\text{fluid}} = \frac{p}{R_g T} \sum_i x_i M_i \quad (3-137)$$

- heat capacity (J/(kg·K))

$$c_{p\text{fluid}} = \frac{\sum_i x_i C_{p,i}}{\sum_i x_i M_i} \quad (3-138)$$

- thermal conductivity (W/(m·K)) as described in Ref. 18

$$k_{\text{fluid}} = \frac{1}{2} \left[\sum_{i=1} x_i k_i + \left(\sum_{i=1} \frac{x_i}{k_i} \right)^{-1} \right] \quad (3-139)$$

In these equations, ρ denotes density (kg/m³), p pressure (Pa), T temperature (K), x mole fraction, M molecular weight (kg/mol), c_p heat capacity per unit mass (J/(kg·K)), C_p represents the heat capacity per mole (J/(mol·K)), and k the thermal conductivity (W/(m·K)).

The third and final area in the **Export to COMSOL Multiphysics** dialog box is the **Export momentum balance** area, which again consists of the **Settings** and the **Variables** pages.

Note: The export of momentum balances is available for 2D and 3D geometries.

This area's functionality is the same as for the **Export energy balance** area described earlier. The expressions listed on the **Variables** page depend on your selection in the **Application mode** list. You can set up the following application modes:

- Incompressible Navier-Stokes
- Weakly compressible Navier-Stokes
- General Laminar Flow

Once the Incompressible Navier-Stokes application mode is exported to COMSOL Multiphysics, you can convert this application mode into any of the Brinkman Equations, k - ϵ Turbulence Model, or k - ω Turbulence Model application modes. Choose the proper settings in the **Application Mode Properties** dialog, found by selecting **Properties** under the **Physics** menu in COMSOL Multiphysics.

If you are modeling solutions with nonconstant density, you should select the Weakly compressible Navier-Stokes application mode, even when your system is isothermal. For reacting multicomponent mixtures, the following mixture properties are defined:

- density (kg/m³)

$$\rho_{\text{fluid}} = \frac{p}{R_g T} \sum_i x_i M_i \quad (3-140)$$

- viscosity (Ns/m²); from Ref. 19

$$\eta_{\text{fluid}} = \frac{\sum_i x_i \eta_i}{\sum_{j=1} x_j \phi_{ij}} \quad (3-141)$$

where

$$\phi_{ij} = \frac{\left[1 + \left(\frac{\eta_i}{\eta_j} \right)^{0.5} \left(\frac{M_j}{M_i} \right)^{0.25} \right]^2}{\left[8 \left(1 + \frac{M_i}{M_j} \right) \right]^{0.5}} \quad (3-142)$$

In these equations η denotes the dynamic viscosity (Ns/m²).

If you only want to export mass balances with one or none of the energy and momentum balances, clear one or both of the check boxes in the upper corners of the **Export energy balance** and **Export momentum balance** areas to obtain the desired export combination.

Export to the COMSOL Script Workspace

You can export a model to the COMSOL Script workspace to run models from the command line, perform parametric studies and advanced postprocessing, or to calibrate and validate a model using experimental data.

Reaction models are exported to the COMSOL Script workspace in the form of a data structures, denoted REL structures. A data structure is an array of containers for a set of fields, which you can access with a dot notation. Choose **File>Export>REL Structure as 'rel'** to export the current reaction model as a REL structure called `rel1`. If you want to specify the name of the exported REL structure, choose **File>Export>REL Structure**.

Select **Export>Simulation data** to export the output from a simulation in the Reaction Engineering Lab to the COMSOL Script workspace. The simulation results are stored in a data structure with three fields, on the following predefined format: The first field is the vector `x`, typically containing simulation times at which results were stored. The second field is a matrix `y`, whose columns typically contain simulation results evaluated at the times specified in `x`. The third field, `legend`, contains a cell array of strings of

the same size as the number of columns in *y*. Note that the data structure for export of simulation data has the same format as the structure for loading experimental data.

Exporting Images

To export the current plot as an image select the menu item **File>Export>Image**. Using the **Export Image** dialog box, you can control font sizes, line widths, and what to include in the image you export. To speed up the image-generation process, a preview feature and image rendering information are available.

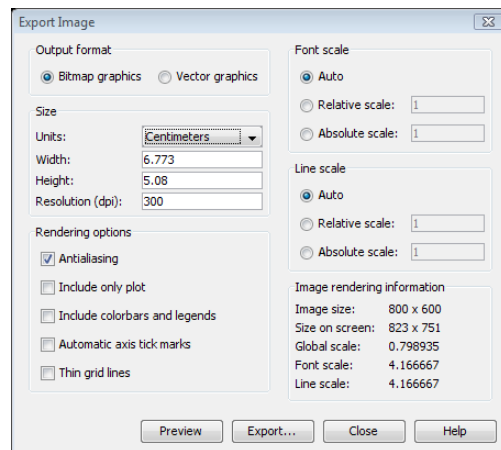


Figure 3-39: The *Export Image* dialog box.

In the **Output format** area, click the **Bitmap graphics** button to export an image using a bitmap-based formats such as TIFF and JPEG. You select the format after clicking the **Export** button. Click the **Vector graphics** button to save the image as an EPS file (Encapsulated PostScript).

In the **Image size** area, you can specify the size of the image. Select the unit from the **Units** list: inches, centimeters, or pixels (pixels are available for bitmap graphics only).

When using inches or centimeters, you can set the size using the **Width**, **Height**, and **Resolution (dpi)** edit fields. When you use pixels as the unit, the **Resolution (dpi)** edit field is not available

The settings in the **Font scale** and **Line scale** areas affect the scaling between the plot's size on the screen and the size in the image (size = number of pixels):

- Click **Auto** to use the global scale (you see its value in the **Image rendering information** area, it is the scale between the size of the plot on screen and the size of the image) if you specify the size in pixels (the software scales text, lines, and other graphics equally). If you specify the size in centimeters or inches, the automatic scale is based on the resolution that you. The font size and line width that you specify when creating the plot should be preserved if you export an image using a certain resolution in dpi (dots per inch) and import it to a document as an image using the same dpi number (a text with a certain size in the plot will look like a text with the same size in the document).
- Click **Relative scale** to use a total font scale that is the automatic scale times the relative scale that you specify.
- Click **Absolute scale** to use a total font scale that is equal to the absolute scale that you specify.

The following settings are available in the **Rendering options** area:

- Select the **Antialiasing** check box to reduces stairstep-like lines (jaggies) and makes lines and edges look smooth
- Select the **Include Only Plot** check box to include only the graphics objects in the drawing area, excluding colorbars, axes, tick marks, titles, and labels.
- Select the **Include Colorbars and Legends** check box to include colorbars and legends, if present.
- Select the **Automatic axis tick marks** check box to take advantage of a new feature that can hide axis tick marks if they overlap. Clear this check box if you want make sure that the image has the same axis tick marks as you see on the screen.
- Select the **Thin grid lines** check box to render thin grid lines compared to other lines in the image. Use this option if you think that the grid is too dominating in the image.

References

1. H.G. Rackett, *J. Chem. Eng. Data*, vol. 15, p. 514, 1970.
2. R.H. Perry and D.W. Green, *Perry's Chemical Engineering Handbook*, 7th ed. McGraw Hill, 1997.
3. B.E. Poling, J.M. Prausnitz, and J.P. O'Connell, *The Properties of Gases and Liquids* 5th ed. McGraw Hill, 2000.
4. M. Zabransky, V. Ruzicka Jr., V. Majer, and E.S. Dolmaski, *J. Phys. Chem. Ref. Data*, Monograph No. 6, Vol. I and II, 1996.
5. S. Gordon and B.J. McBride, *Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouquet Detonations*, NASA-SP-273, 1971.
6. See, for instance, www.me.berkeley.edu/gri_mech/data/nasa_plnm.html.
7. P.D. Neufeld, A.R. Janzen, and R.A. Aziz, *J. Chem. Phys.*, vol. 57, p. 1100, 1972.
8. R.S. Brokaw, *Ind. Eng. Process Design Develop.*, vol. 8, p. 240, 1969.
9. C.R. Wilke and P. Chang, *AIChE J.*, vol. 1, p. 264, 1955.
10. W.R. Gambill, *Chem. Eng.*, vol. 66, p. 129, 1959.
11. L.I. Stiel and G. Thodos, *AIChE J.* vol. 10, p. 26, 1964.
12. P.M. Brown, A.C. Hindmarsh, and L.R. Petzold, *SIAM J. Sci. Comput.*, vol. 15, p. 1467, 1994.
13. R.J. Kee, F.M. Rupley, and J.A. Miller, *Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics*, Sandia National Laboratories Report SAND89-8009, 1990.
14. See, for instance, <http://www.comsol.com/reaction>
15. F. Lindemann, *Trans. Faraday Soc.*, vol. 17, p. 598, 1922.
16. R.G. Gilbert, K. Luther, and J. Troe, *Ber. Bunsenges. Phys. Chem.*, vol. 87, p. 169, 1983.
17. P.H. Stewart, C.W. Larson, and D.M. Golden, *Combustion and Flame*, vol. 75, p. 25, 1989.

18. Y.S. Touloukian, P.E. Liley, and S.C. Saxena, *Thermophysical Properties of Matter, Vol. 3, Thermal Conductivity*, IFI/Plenum, Washington, 1970, p. 45.
19. C.R. Wilke, *J. Chem. Phys.*, vol. 18, p. 517, 1950.

Model Library

Introduction

Model Library Guide

The table below summarizes key information about the models in the Model Library chapter and Modeling Strategy chapters of this manual.

TABLE 4-1: COMSOL REACTION ENGINEERING LAB MODEL LIBRARY

MODEL	PAGE	COMSOL SOFTWARE COMBINATION	MASS BALANCE	ENERGY BALANCE	MOMENTUM BALANCE	CHEMKin IMPORT	EXPORT TO SCRIPT	EXPORT TO MULTIPHYSICS
MODEL NAME								
Isothermal HI Reactor	9	Reaction Engineering Lab	√					
Nonisothermal HI Reactor	15	Reaction Engineering Lab	√	√				
Space-dependent HI Reactor	23	Reaction Engineering Lab Chemical Engineering Module	√	√				√
Parameter Estimation Isothermal	30	Reaction Engineering Lab	√					
Parameter Estimation Nonisothermal	35	Reaction Engineering Lab	√					
Parameter Estimation Reaction Order	41	Reaction Engineering Lab	√					
Parameter Estimation CO Adsorption	44	Reaction Engineering Lab	√					
DNA Degradation	154	Reaction Engineering Lab Script	√					

TABLE 4-1: COMSOL REACTION ENGINEERING LAB MODEL LIBRARY

MODEL	PAGE	COMSOL SOFTWARE COMBINATION	MASS BALANCE	ENERGY BALANCE	MOMENTUM BALANCE	CHEMICAL IMPORT	EXPORT TO SCRIPT	EXPORT TO MULTIPHYSICS
Drug Release	163	Reaction Engineering Lab Chemical Engineering Module	√					√
Enzyme Inhibition	180	Reaction Engineering Lab	√					
Ozone Combustion	187	Reaction Engineering Lab Chemical Engineering Module	√	√	√			√
Diesel Filter	205	Reaction Engineering Lab Chemical Engineering Module	√	√	√			√
NOx Reduction	234	Reaction Engineering Lab Chemical Engineering Module	√		√	√		√
Compression Ignition	258	Reaction Engineering Lab	√	√		√		
Pesticide Transport	271	Reaction Engineering Lab Earth Science Module	√		√			√
Oscillating Reactions	289	Reaction Engineering Lab Script	√				√	
Pressure-Time Data in Parameter Estimation	305	Reaction Engineering Lab	√					

TABLE 4-1: COMSOL REACTION ENGINEERING LAB MODEL LIBRARY

MODEL	PAGE	COMSOL SOFTWARE COMBINATION	MASS BALANCE	ENERGY BALANCE	MOMENTUM BALANCE	CHEM KIN IMPORT	EXPORT TO SCRIPT	EXPORT TO MULTIPHYSICS
Microbial Growth	312	Reaction Engineering Lab Script	√				√	
Tortuous Reactor	320	Reaction Engineering Lab MEMS Module	√		√			√
Ibuprofen Synthesis	336	Reaction Engineering Lab	√					
Protein Adsorption	347	Reaction Engineering Lab Chemical Engineering Module	√					√
Chlorine Scrubber	359	Reaction Engineering Lab	√					
Non-Isothermal Plug-Flow	367	Reaction Engineering Lab	√	√		√		
Semibatch Polymerization	380	Reaction Engineering Lab	√					
CSTR Startup	388	Reaction Engineering Lab	√	√				
Fluid Catalytic Cracking	399	Reaction Engineering Lab	√					
Carbon Deposition	408	Reaction Engineering Lab Chemical Engineering Module	√		√			√
Pentaerythritol Kinetics	430	Reaction Engineering Lab	√					

TABLE 4-1: COMSOL REACTION ENGINEERING LAB MODEL LIBRARY

MODEL	PAGE	COMSOL SOFTWARE COMBINATION	MASS BALANCE	ENERGY BALANCE	MOMENTUM BALANCE	CHEM KIN IMPORT	EXPORT TO SCRIPT	EXPORT TO MULTIPHYSICS
Cinnamaldehyde Hydrogenation	442	Reaction Engineering Lab	√					
GaAs CVD	453	Reaction Engineering Lab Chemical Engineering Module	√	√	√			√

Degradation of DNA in Plasma

Introduction

Biotechnology is a rapidly growing area in the pharmaceutical sciences. One example of a clinical application is gene therapy, where it is possible to produce proteins *in vivo*, using the body's own mechanisms for protein production. Major issues in gene delivery involve the transport of plasmid DNA (pDNA) to target sites and the conversion between different forms of pDNA.

The following example illustrates the kinetic analysis of pDNA degradation. Relying on a proposed first-order reaction mechanism, you first evaluate experimental data to find the rate constants. Making use of these constants, you then set up the kinetic model in the Reaction Engineering Lab, which solves the corresponding material balance equations. As a final verification, you can compare the modeling results with experimental data you load into the Reaction Engineering Lab.

Introduction

pDNA can be used to express proteins in the human body, proteins that can have therapeutic effects. It exists in three forms with varying protein-expression rates. These different pDNA-forms interconvert and degrade with time. As a consequence, an overall therapy benefits from knowledge about the distribution of pDNA-forms over time. The following example investigates a mechanism for pDNA degradation and compares the modeling results with experimental data (Ref. 1).

Model Description

pDNA exists in three forms: a supercoiled form (SC), an open-circular form (OC), and a linear form (L). The protein expression rate for the SC form is greater than the one for the OC form, which in turn is significantly greater than that for the L form. The kinetic model in this study assumes that the pDNA-forms interconvert and decompose according to the mechanism in Figure 4-1.

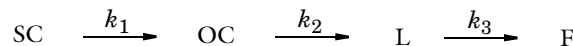


Figure 4-1: Kinetic model of plasmid DNA interconversion and decomposition. Supercoiled pDNA (SC) converts to an open-circular form (OC), which in turn converts to a linear form (L). The linear pDNA decomposes to form linear fragments (F).

This model proposes a set of irreversible reactions in which SC-form pDNA converts to the OC form and subsequently to the L form. Then the L-form decomposes into a number of linear fragments, collectively denoted as F.

The three irreversible reactions in Figure 4-1 translate into the following reaction rate expressions:

$$r_1 = k_1 c_{SC} \quad (4-1)$$

$$r_2 = k_2 c_{OC} \quad (4-2)$$

$$r_3 = k_3 c_L \quad (4-3)$$

Making use of the reaction rates (Equation 4-1 to Equation 4-3) and the reaction stoichiometry, the material balances for the model become:

$$\frac{dc_{SC}}{dt} = -k_1 c_{SC} \quad (4-4)$$

$$\frac{dc_{OC}}{dt} = k_1 c_{SC} - k_2 c_{OC} \quad (4-5)$$

$$\frac{dc_L}{dt} = k_2 c_{OC} - k_3 c_L \quad (4-6)$$

$$\frac{dc_F}{dt} = k_3 c_L \quad (4-7)$$

The Reaction Engineering Lab automatically generates these reaction-rate expressions and balance equations; all you need to do is to type the corresponding chemical reaction formulas into the user interface. This specific system is assumed to be isothermal, which is often the case for biological systems. To solve the model, the Reaction Engineering Lab needs the rate constants and initial species concentrations (10 ng/ μ L for the SC form) as input.

The rate constants k_1 through k_3 have to be evaluated from experimental data, summarized below:

TIME (s)	c_{SC} (ng/ μ L)	c_{OC} (ng/ μ L)	c_L (ng/ μ L)
0	10	0	0
60	5.0	4.1	0.1

TIME (s)	c_{SC} (ng/ μL)	c_{OC} (ng/ μL)	c_{L} (ng/ μL)
120	3.5	6.5	0.3
180	1.1	7.0	0.5
300	0.5	8.1	0.8
420	0.1	8.0	1.2
600	0	7.8	1.7
900	0	7.1	2.4
1200	0	6.3	2.5
1800	0	4.5	2.6
2400	0	3.0	2.0
3000	0	2.1	1.8
3600	0	1.5	1.2

In this example you will use an integral approach to calculate the rate constants from the experimental data. This involves reformulating the reaction rate equations by means of integration. Equation 4-4 through Equation 4-6 become:

$$c_{\text{SC}}(t_m) - c_{\text{SC}}(t_0) = -k_1 \int_{t_0}^{t_m} c_{\text{SC}} dt \quad (4-8)$$

$$c_{\text{OC}}(t_m) - c_{\text{OC}}(t_0) = k_1 \int_{t_0}^{t_m} c_{\text{SC}} dt - k_2 \int_{t_0}^{t_m} c_{\text{OC}} dt \quad (4-9)$$

$$c_{\text{L}}(t_m) - c_{\text{L}}(t_0) = k_2 \int_{t_0}^{t_m} c_{\text{OC}} dt - k_3 \int_{t_0}^{t_m} c_{\text{L}} dt \quad (4-10)$$

For each time interval, $t_0 \leq t \leq t_m$, evaluate the concentration differences and integrals numerically in COMSOL Script and solve the system of equations

$$\begin{bmatrix} D_{\text{SC}} \\ D_{\text{OC}} \\ D_{\text{L}} \end{bmatrix} = \begin{bmatrix} -S_{\text{SC}} & 0 & 0 \\ S_{\text{SC}} & -S_{\text{OC}} & 0 \\ 0 & S_{\text{OC}} & -S_{\text{L}} \end{bmatrix} \begin{bmatrix} k_1 \\ k_2 \\ k_3 \end{bmatrix} \quad (4-11)$$

where for each species (i)

$$D_i = c_i(t_m) - c_i(t_0) \quad (4-12)$$

$$S_i = \int_{t_0}^{t_m} c_i dt \quad (4-13)$$

Because the system given by Equation 4-11 is overdetermined, **k** is the least-squares solution.

Results

The following rate constants were calculated from the experimental data and reaction mechanism:

$k_1 (s^{-1})$	$k_2 (s^{-1})$	$k_3 (s^{-1})$
$1.0 \cdot 10^{-2}$	$5.0 \cdot 10^{-4}$	$1.0 \cdot 10^{-3}$

Figure 4-2 shows the simulation results for the development of pDNA forms as functions of time; it does not display the fragmental products, F.

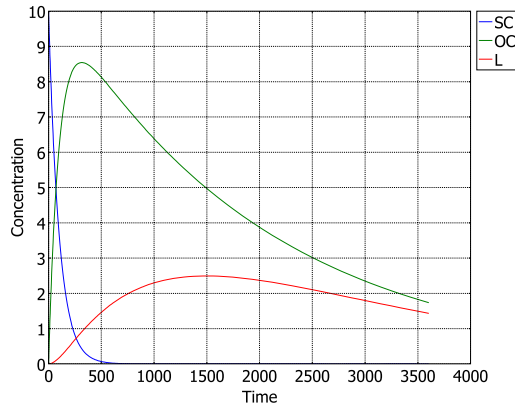


Figure 4-2: pDNA species concentrations given in ng/μL as functions of time (s).

Figure 4-3 shows the experimental values in the same plot as the simulation results. Clearly, the assumptions of the kinetic model are in agreement with the experimental findings.

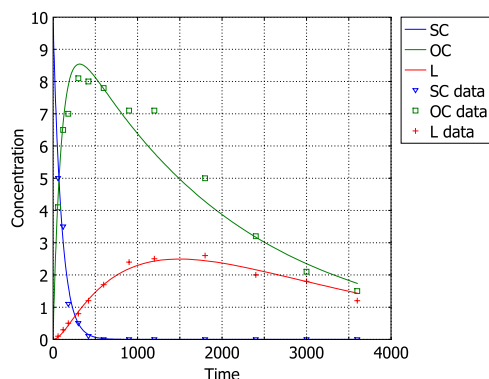


Figure 4-3: A plot resulting from reading in experimental data and comparing it to simulation results.

The estimated rate constants show that the supercoiled pDNA rapidly transforms into the open-circular form with a half-life of approximately 1.2 minutes:

$$t_{1/2} = \frac{\ln 2}{k}$$

The open-circular and linear pDNA decay with half-lives of 23.1 and 11.5 minutes, respectively. As previously mentioned, the supercoiled pDNA has the highest protein-expression rate of the three forms. However, because the SC form has a half-life of only 1.2 minutes, it is likely that it decomposes during transport to the therapeutic target sites. These findings imply that you have to find ways to hinder the relatively fast decay of SC.

In conclusion, this example sets up a kinetic model for the transformation and degradation of pDNA in the Reaction Engineering Lab. It uses COMSOL Script and the Reaction Engineering Lab to validate a kinetic model and estimate the rate constants in the proposed kinetic mechanism.

Reference

1. B.E. Houk, G. Hochhaus, and J.A. Hughes, *AAPS Pharmsci*, vol. 1, p. 1, 1999.

Modeling Using COMSOL Script

MODEL NAVIGATOR

1 Start **COMSOL Script**.

2 In the **COMSOL Script** window, create a time vector by typing the following line at the prompt, then press Enter.

```
t = [0 60 120 180 300 420 600 900 1200 1800 2400 3000 3600];
```

3 Use the following lines of code to create vectors with the concentration data:

```
c_sc = [10 5 3.5 1.1 0.5 0.1 0 0 0 0 0 0 0]';  
c_oc = [0 4.1 6.5 7.0 8.1 8.0 7.8 7.1 6.3 4.5 3.2 2.0 1.5]';  
c_l = [0 0.1 0.3 0.5 0.8 1.2 1.7 2.4 2.5 2.6 2.0 1.8 1.2]';
```

4 With reference to Equation 4-12, create the concentration difference vectors:

```
d_sc = c_sc - c_sc(1);  
d_oc = c_oc - c_oc(1);  
d_l = c_l - c_l(1);
```

5 With reference to Equation 4-13, evaluate the integrals using the trapezoidal rule:

```
s_sc = cumtrapz(t, c_sc);  
s_oc = cumtrapz(t, c_oc);  
s_l = cumtrapz(t, c_l);
```

6 Create a vector of zeros with the same number of elements as the data vectors:

```
z = zeros(1, length(t))';
```

7 With reference to Equation 4-11, create the vector **D**:

```
D = [d_sc; d_oc; d_l];
```

8 With reference to Equation 4-11, create the matrix **S**:

```
S = [[-s_sc z z]; [s_sc -s_oc z]; [z s_oc -s_l]];
```

9 Solve for the vector **k** of Equation 4-11,

```
k = S \ D
```

to obtain the following rate constants:

```
k =
```

```
0.0100
```

```
5.0e-004
1.0e-003
```

With the subsequent three steps you create a data structure called `dna` and fill it with the experimental values. You will later import the data into the Reaction Engineering Lab.

- 10** Store the time data in the `x` vector of the `dna` data structure:

```
dna.x=t;
```

- 11** Store the concentration data as columns in the `y` matrix of the `dna` data structure:

```
dna.y=[c_sc c_oc c_l];
```

- 12** Enter labels for the various columns of data with the following line, which defines entries in the cell array `legend` for the `dna` structure data; then press Enter.

```
dna.legend={'SC data', 'OC data', 'L data'};
```

- 13** Start the Reaction Engineering Lab by choosing **File>Reaction Engineering Lab**.

- 14** Keep the COMSOL Script window open and click on the Reaction Engineering Lab user interface.

Modeling Using COMSOL Reaction Engineering Lab

REACTIONS INTERFACE

- 1** From the **Model** menu, select **Reaction Settings**.
- 2** Create three entries in the **Reaction selection** list by clicking the **New** button three times.
- 3** Enter the reaction formulas in the table below by first selecting the appropriate row in the **Reaction selection** list and then typing the text in the **Formula** edit field. Note how the Reaction Engineering Lab automatically generates expressions for the reaction rates and presents them in the **r** edit field.

REACTION ID #	REACTION FORMULA
1	SC=>OC
2	OC=>L
3	L=>F

When you type the reaction formulas, the reactions are automatically activated and the corresponding check boxes become selected; no separate action is required to activate the reactions.

- 4 Enter the following values for the **Forward rate constant** by first selecting the appropriate row in the **Reaction selection** list and then typing the corresponding number in the **k^f** edit field:

REACTION ID #	k ^f
1	1e-2
2	5e-4
3	1e-3

SPECIES INTERFACE

- 1 While still in the **Reaction Settings** dialog box, click the **Species** tab.
- 2 Verify that the **Species selection** list has the four species (SC, OC, L, and F).
- 3 On the **General** page, enter the following initial concentrations, one by one, in the **c₀** edit field after first having selected the appropriate entry in the **Species selection** list:

SPECIES NAME	c ₀
SC	10
OC	0
L	0
F	0

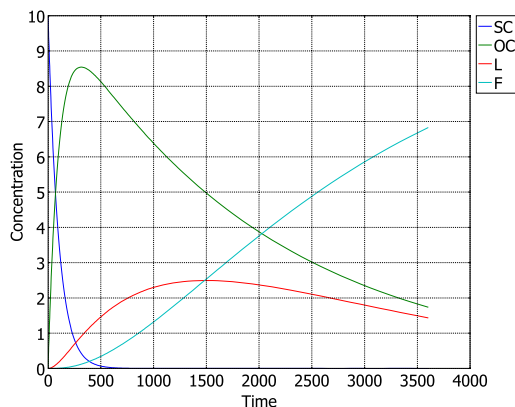
- 4 Click **Close**.

COMPUTING THE SOLUTION

- 1 Open the **Simulation>Solver Parameters** dialog box.
- 2 Type 3600 in the **Times** edit field.
- 3 Click **OK**.
- 4 Click the **Solve Problem** button (=) on the Main toolbar.

POSTPROCESSING AND VISUALIZATION

The default plot shows the time variations of the concentrations of all four species, as displayed in the figure below:



To create Figure 4-2 on page 157 follow these steps:

- 1 Choose **Postprocessing>Plot Parameters** (or click the corresponding button on the Main toolbar).
- 2 Select F in the **Quantities to plot** list and click the < button to remove it from the plot.
- 3 Click **OK**.

Now, read the experimental data into the Reaction Engineering Lab and compare with the simulation results.

- 1 Choose **File>Import>Experimental Data From Workspace** to bring up the dialog box.
- 2 Type dna in the **Variable name for structure with experimental data** edit field.
- 3 Click **OK**.
- 4 Choose **Postprocessing>Plot Parameters**.
- 5 Select the **Plot experimental data** check box at the right bottom corner.
- 6 Click **OK** to create Figure 4-3.

Drug Release from a Biomaterial

Introduction

Biomaterial matrices for drug release are useful for *in vivo* tissue regeneration. The following example describes the release of a drug from a biomaterial matrix to damaged cell tissue. Specifically, a nerve guide delivers a regenerating drug to damaged nerve ends. The model examines detailed drug-release kinetics with rate expressions handling drug dissociation/association reactions as well as matrix degradation by enzyme catalysis. The enzyme reaction is described by Michaelis-Menten kinetics. With this simulation it is easy to investigate design parameters governing the rate of drug release such as drug-to-biomaterial affinity, biomaterial degradation, drug loading, and of course the influence of geometry and composition of the biomaterial matrix. The model illustrates the use of the Reaction Engineering Lab and the Chemical Engineering Module as powerful modeling tools for bioengineering applications.

Model Definition

In this model a drug is released into a region containing damaged nerve ends. The biomaterial holding the drug has a cylindrical shape and serves a dual purpose: It acts as a guide to help regenerating nerve cells connect, and it also stimulates the healing process through targeted drug release.

The model simulates transient chemical reactions and species transport in a 2D geometry with axial symmetry.

Figure 4-4 shows the full 3D geometry as well as the 2D modeling domain, reduced by axial symmetry and a mirror plane. The subdomains are:

- The nerve-cell tissue (Ω_1)

- The biomaterial matrix (Ω_2)
- The surrounding medium (Ω_3)

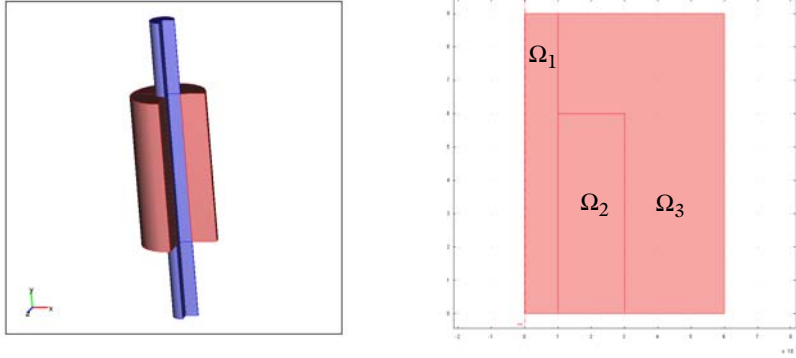


Figure 4-4: The full 3D geometry (left) and the equivalent modeling domain reduced to 2D by axial symmetry (right). The subdomains are: the nerve-cell tissue (Ω_1), the biomaterial matrix (Ω_2), and the surrounding medium (Ω_3).

In the biomaterial matrix, a drug molecule, d , binds to a peptide, p , which in turn is anchored to the matrix, m . Matrix-bound species are labeled mpd and mp , respectively, the latter referring to a species where no drug is bound to the peptide. Species mpd and mp are active only in subdomain Ω_2 .

Two mechanisms release the drug from the matrix. First, the drug can simply dissociate from the matrix site mp . Second, matrix degradation by an enzyme, e , originating from the cell-tissue domain, leads to release of the drug-peptide species, pd , from which the drug subsequently dissociates. The unbound species p , d , pd , and e are active in the entire model domain. Figure 4-5 illustrates the complete reaction scheme.

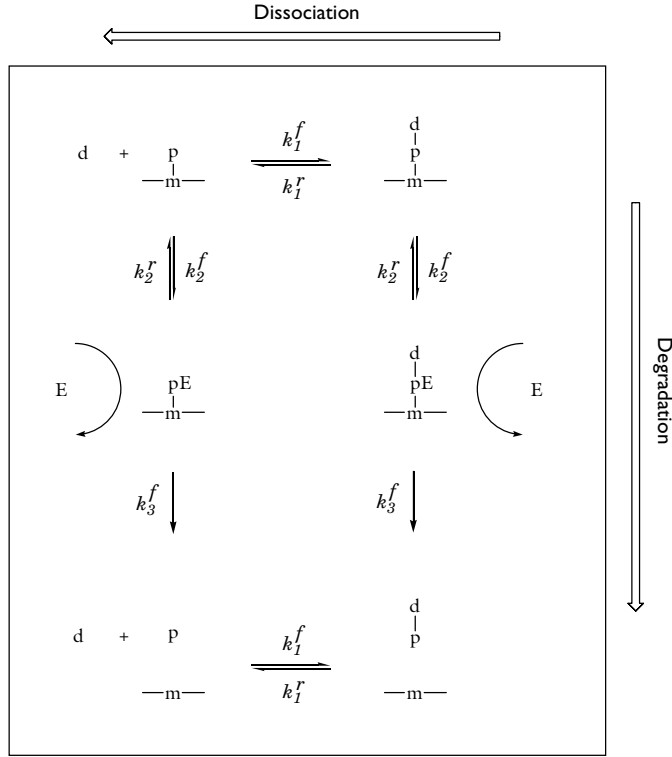


Figure 4-5: Reaction scheme describing drug dissociation/association reactions (horizontal) and matrix-degradation reactions (vertical).

The simulation makes use of two diffusion application modes in the Chemical Engineering Module. The time-dependent mass balance per species is described by

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_{ik} \nabla c_i) = R_{ik} \quad \text{in } \Omega_k \quad (4-14)$$

where D_{ik} (m^2/s) is the diffusion coefficient for species i in the medium of subdomain Ω_k . Further, R_{ik} ($\text{mol}/(\text{m}^3 \cdot \text{s})$) is the rate expression for species i in the medium of subdomain Ω_k . In the matrix subdomain, all the reactions described in Figure 4-5 are possible, leading to the following rate expressions:

$$R_{d2} = -k_1^f c_d (c_{mp} + c_p) + k_1^r (c_{mpd} + c_{pd}) \quad (4-15)$$

$$R_{p2} = -k_1^f c_d c_p + k_1^r c_{pd} + R_{MMmp} \quad (4-16)$$

$$R_{pd2} = k_1^f c_d c_p - k_1^r c_{pd} + R_{MMmpd} \quad (4-17)$$

$$R_{mp2} = -k_1^f c_d c_{mp} + k_1^r c_{mpd} - R_{MMmp} \quad (4-18)$$

$$R_{mpd2} = k_1^f c_d c_{mp} - k_1^r c_{mpd} - R_{MMmpd} \quad (4-19)$$

The rate terms R_{MMmp} and R_{MMmpd} refer to the Michaelis-Menten kinetics describing the enzyme catalyzed degradation of the matrix:

$$R_{MMmp} = \frac{V_{\max} c_{mp}}{K_M + c_{mp}}$$

$$R_{MMmpd} = \frac{V_{\max} c_{mpd}}{K_M + c_{mpd}}$$

with

$$V_{\max} = k_3^f c_e$$

$$K_M = \frac{k_3^f + k_2^r}{k_2^f}$$

R_{MMmp} describes the disappearance of mp sites and the production of p species.

R_{MMmpd} describes the disappearance of mpd sites and the production of pd species. In the cell region (Ω_1) and in the surrounding medium (Ω_3) only dissociation/association reactions occur, leading to the rate expressions

$$R_{d1} = R_{d3} = R_{p1} = R_{p3} = -k_1^f c_d c_p + k_1^r c_{pd}$$

$$R_{pd1} = R_{pd3} = k_1^f c_d c_p - k_1^r c_{pd}$$

The boundary condition is axial symmetry along the rotational axis and insulation/symmetry elsewhere. Values for diffusion coefficients and rate constants come from the literature (Ref. 1).

Results and Discussion

Figure 4-6 shows the concentration transients of the reacting species in a perfectly mixed (space-independent) system.

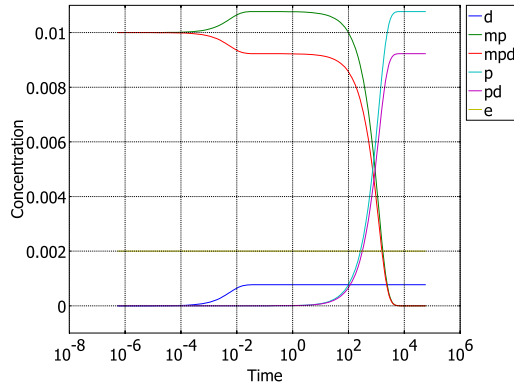


Figure 4-6: Concentrations of all reacting species (mol/m^3) as functions of time (s).

The effect of enzyme degradation is clearly visible, with matrix-bound peptide species (mp and mpd) decreasing and free peptide species (p and pd) increasing with time. The matrix is completely degraded after approximately 5000 seconds. As the drug and peptide species have the same association/dissociation kinetics, no matter whether the peptide is free or matrix-bound, the steady-state concentration of drug is constant during the degradation process.

Solving the space-dependent mass balances of Equation 4-14 results in concentration distributions of all participating species as functions of time. Figure 4-7 shows the concentration of drug across the modeling domain.

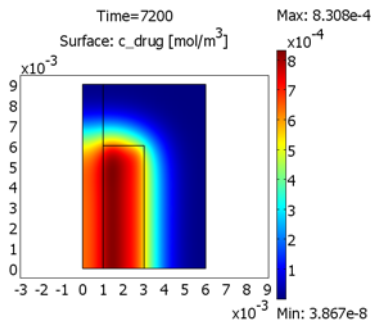


Figure 4-7: Drug concentration at the end of the simulation (7200 s).

You can visualize the effect of matrix degradation on the release of the drug by plotting the total drug concentration over a cross section of the matrix as a function of time.

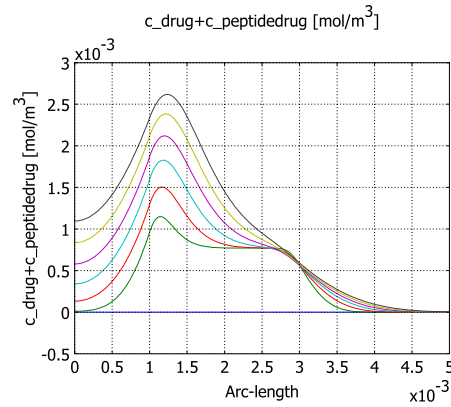


Figure 4-8: Concentration profiles describing the total drug concentration ($c_d + c_{pd}$) across the modeling domain. Profiles were collected at times up to 3600 s.

As noted earlier, the enzyme originates from the nerve-cell subdomain. From Figure 4-8 it is clear that matrix degradation has a directing effect on the drug release toward the damaged cell region.

To visualize the degradation front passing through the biomaterial geometry, plot the total matrix site concentration ($c_{mp} + c_{mpd}$) across the matrix subdomain (Figure 4-9).

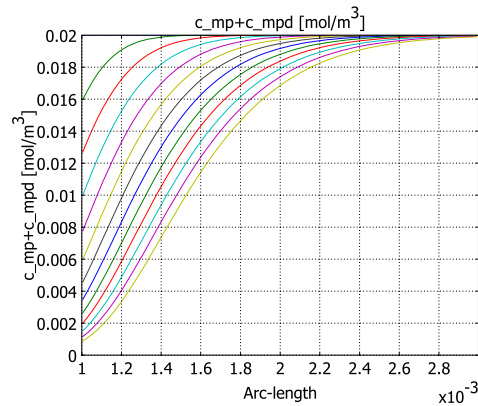


Figure 4-9: Concentration profiles describing the total matrix site concentration ($c_{mp} + c_{mpd}$) with profiles collected at times up to 7200 s.

The detailed reaction/transport description in this model allows for the investigation of many design parameters relevant to bioengineering. This case presents the effect of matrix degradation on drug release as a function of time and geometry. Furthermore, it is straightforward to study the influence of the drug/peptide affinity by varying the rate constants k_1^f and k_1^r , or the influence of drug loading by varying the $c_{mp}:c_{mpd}$ ratio. Of course, the ability to examine alternative geometries and mixed biomaterial domains gives even more design flexibility.

Reference

1. D.J. Maxwell, B.C. Hicks, S. Parsons, and S.E. Sakiyama-Elbert, *Acta Biomat.*, vol. 1, p. 101, 2005.

Note: The complete model requires the Chemical Engineering Module and COMSOL Multiphysics.

Model Library path: Biochemistry/drug_release1

Model Library path: Biochemistry/drug_release2

The following path shows the location of the COMSOL Multiphysics model:

Model Library path:

Reaction_Engineering_Lab/Biochemistry/drug_release2

Modeling Using COMSOL Reaction Engineering Lab

To set up this model, enter the chemistry described in Figure 4-5 into the Reaction Engineering Lab in two steps. First describe the association/dissociation chemistry by entering the corresponding chemical reaction formulas. Second, for the degradation

of the biomaterial matrix due to enzyme catalysis, directly enter the well-known expressions for the Michaelis-Menten rates.

MODEL NAVIGATOR

Start the Reaction Engineering Lab. In the **Model Navigator**, click the **New** button.

OPTIONS AND SETTINGS

- 1 Click the **Model Settings** button on the Main toolbar.
- 2 In the **Reacting fluid** list, select **Liquid**.
- 3 Select the **Calculate thermodynamic properties** check box.
- 4 Select the **Calculate species transport properties** check box.
- 5 In the **T** edit field, type 310.
- 6 Click **Close**.
- 7 Choose **Model>Constants**, then define the following names and expressions. Note that K_m is the Michaelis-Menten constant.

NAME	EXPRESSION
kf_mm3	7.336e-3
Km	0.01

- 8 Click **OK**.
- 9 Choose **Model>Expressions**, then define the Michaelis-Menten expressions by entering the following settings:

NAME	EXPRESSION
Vmax	kf_mm3*c_e
R_mm_mp	Vmax*c_mp/(Km+c_mp)
R_mm_mpd	Vmax*c_mpd/(Km+c_mpd)

- 10 Click **OK**.

REACTIONS INTERFACE

- 1 Choose **Model>Reaction Settings**.
- 2 On the **Reactions** page, create two entries in the **Reaction selection** list by clicking the **New** button twice.

- Enter the following reaction formulas by first selecting the appropriate row in the **Reaction selection** list and then typing the text in the **Formula** edit field:

REACTION ID #	REACTION FORMULA
1	d+mp<=>mpd
2	d+p<=>pd

- On the **Kinetics** page, enter the following forward and reverse rate constants. To do so, first select the appropriate row in the **Reaction selection** list, and then enter the numbers in the appropriate edit fields. Note how you set the rate constants of Reaction 2 equal to those of Reaction 1 by invoking the variable names corresponding to the **Rate constant** edit fields, kf_1 and kr_1.

REACTION ID #	k ^f	k ^r
1	1.5e4	13.5
2	kf_1	kr_1

SPECIES INTERFACE

- Click the **Species** tab.
- Look at the **Species selection** list and note the five species that result automatically when you enter the reaction formulas as described earlier.
- Create a new species entry by clicking **New**, then in the **Formula** edit field enter **e**. This entry corresponds to the enzyme.
- Go to the **General** tab. For each entry in the **Species selection** list, type the following initial concentrations in the **c₀** edit field:

SPECIES NAME	c ₀
d	0
mp	1e-2
mpd	1e-2
p	0
pd	0
e	2e-3

To include the effects of the enzyme degradation into the kinetic description, you must modify the predefined reaction expressions with the Michaelis-Menten rates, which you defined earlier in the scalar expressions.

- 5 While still on the **General** page, select the appropriate entry in the **Species selection** list and modify the rate expressions in the corresponding **R** edit field.

SPECIES NAME	R
mp	$-r_1 - R_{mm_mp}$
mpd	$r_1 - R_{mm_mpd}$
p	$-r_2 + R_{mm_mp}$
pd	$r_2 + R_{mm_mpd}$

- 6 Click the **Transport** tab.
- 7 For each species in the list below, select the corresponding entry in the **Species selection** list. Then select the **Specify diffusivity** check box and type the appropriate diffusivity value in the **D⁰** edit field.

SPECIES NAME	D ⁰
d	8.93e-11
mp	0
mpd	0
p	1.58e-10
pd	8.3e-11
e	5e-11

- 8 Click **Close**.

Start by investigating the kinetics in a perfectly mixed system in the Reaction Engineering Lab.

COMPUTING THE SOLUTION

Click the **Solve Problem** button (=) on the Main toolbar.

POSTPROCESSING

To reproduce results of Figure 4-6, click the **x log** button on the Main toolbar.

To reproduce results of Figure 4-7, follow the steps listed below.

SPECIES INTERFACE

- 1 Choose **Model>Reaction Settings**.
- 2 Click the **Species** tab.
- 3 Go to the **General** tab.

- 4 Choose the species **e** from the **Species selection** list and type 0 in the **c₀** edit field.
You change the value of the initial concentration because the first export of the reaction model is to a geometry domain where the enzyme concentration is zero.
- 5 Click **Close**.

EXPORTING THE MASS BALANCE

- 1 Choose **File>Export>Model to COMSOL Multiphysics**.
- 2 Choose **2D** in the **Space dimension** list, then click **OK**.
This step launches COMSOL Multiphysics and opens the **Export to COMSOL Multiphysics** dialog box, to which the next five steps refer:
- 3 On the **Settings** page in the **Export mass balance** area, select **Diffusion: New** from the **Application mode** list.
- 4 In the **Group name** edit field on the same page, type **biomaterial**.
- 5 Clear the check box at the top of the **Export energy balance** area.
- 6 Clear the check box at the top of the **Export momentum balance** area.
- 7 Click **Export** to close the **Export to COMSOL Multiphysics** dialog box.
- 8 In the Reaction Engineering Lab, choose **File>Save As** and save the current reaction model as **drug_release1.rxn**.

Now create a new reaction model that describes the reaction occurring outside the biomaterial matrix. The reaction to include is the association/dissociation reaction of the unbound peptide with the drug. When entering the reaction formulas, use new species names. You later couple the concentration variables for peptide, drug, peptide-drug complex, and enzyme into COMSOL Multiphysics.

MODEL NAVIGATOR

Create a new reaction model by choosing **File>New**.

OPTIONS AND SETTINGS

- 1 Click the **Model Settings** button on the Main toolbar.
- 2 In the **Reacting fluid** list, select **Liquid**.
- 3 Select the **Calculate thermodynamic properties** check box.
- 4 Select the **Calculate species transport properties** check box.
- 5 In the **T** edit field, type 310.
- 6 Click **Close**.

REACTIONS INTERFACE

- 1 Click the **Reaction Settings** button on the Main toolbar.
- 2 On the **Reactions** page, create an entry in the **Reaction selection** list by clicking the **New** button.
- 3 Type the following data in the **Formula** edit field:

REACTION ID #	REACTION FORMULA
I	$D + P \rightleftharpoons PD$

- 4 Go to the **Kinetics** page and enter the following forward and reverse rate constants:

REACTION ID #	k^f	k^r
I	1.5e4	13.5

SPECIES INTERFACE

- 1 Click the **Species** tab.
In the **Species selection** list, notice the three species that resulted automatically when you entered the reaction formula.
- 2 Create a new species entry by clicking **New**, then type E in the **Formula** edit field. This entry corresponds to the enzyme.
- 3 Click the **Transport** tab.
- 4 Select the appropriate entry in the **Species selection** list, select the **Specify diffusivity** check box, and enter the following diffusivities in the D^0 edit field:

SPECIES NAME	D^0
D	8.3e-11
P	1.68e-10
PD	9.31e-11
E	5.5e-11

- 5 Click **Close**.

Now export these settings to a second application mode in COMSOL Multiphysics. You want to create two separate groups: one corresponding to the conditions in the fluid surrounding the biomaterial and nerve, and another corresponding to the nerve-cell domain.

EXPORTING THE MASS BALANCE

- 1 Choose **File>Export>Model to COMSOL Multiphysics**.

- 2 On the **Settings** page in the **Export mass balance** area, select **Diffusion: New** from the **Application mode** list.
- 3 In the **Group name** edit field on the same page, type **fluid**.
- 4 Clear the check box at the top of the **Export energy balance** area.
- 5 Clear the check box at the top of the **Export momentum balance** area.
- 6 Click **Export** to close the **Export to COMSOL Multiphysics** dialog box.

Now modify the settings of the reaction model to reflect the situation in the nerve-cell region.

SPECIES INTERFACE

- 1 Click the **Reaction Settings** button on the Main toolbar.
- 2 Click the **Species** tab.
- 3 Click the **General** tab, then enter the following initial concentrations, one by one, in the **c₀** edit field after first having selecting the appropriate entry in the **Species selection** list:

SPECIES NAME	c ₀
D	0
P	0
PD	0
E	2e-3

- 4 Click the **Transport** tab.
- 5 For each species in the table below, select the entry in the **Species selection** list and type the corresponding diffusivity value in the **D⁰** edit field:

SPECIES NAME	D ⁰
D	8.93e-11
P	1.58e-10
PD	8.3e-11
E	5e-11

- 6 Click **Close**.

EXPORT SETTINGS

From the **File** menu, choose **Export>Model to COMSOL Multiphysics**.

Export the Mass Balance

- 1 In the **Export mass balance** area, select **Diffusion (chdi2)** from the **Application mode** list.
- 2 In the **Group name** edit field, type **nerve**.
- 3 Go to the **Export energy balance** area and clear the check box at the top.
- 4 Go to the **Export momentum balance** area and clear the check box.
- 5 Click **Export**.
- 6 Choose **File>Save as** and save the current reaction model as **drug_release2.rxn**.

Modeling Using COMSOL Multiphysics

- 1 Switch to **COMSOL Multiphysics**.
- 2 Choose **Multiphysics>Model Navigator**.
- 3 Verify that the model contains two **Diffusion** application modes as a result of the exports from the Reaction Engineering Lab.
- 4 Click **OK**.

GEOMETRY MODELING

- 1 While holding down the Shift key, click the **Rectangle/Square** button on the Draw toolbar. Enter the values for the rectangle **R1** from the following table, then repeat the procedure for the rectangles **R2** and **R3**.

EDIT FIELD	R1	R2	R3
Width	6e-3	1e-3	2e-3
Height	9e-3	9e-3	6e-3
Base	Corner	Corner	Corner
x	0	0	1e-3
y	0	0	0

- 2 Click the **Zoom Extents** button on the Main toolbar.

PHYSICS SETTINGS

Subdomain Settings

- 1 Choose **Multiphysics>1 Diffusion (chdi)**.
- 2 Choose **Physics>Subdomain Settings**.
- 3 From the **Subdomain selection** list, select **1**, then clear the **Active in this domain** check box. Repeat this procedure for Subdomain 3.

- 4 From the **Subdomain selection** list, select **2**.
- 5 From the **Group** list, select **biomaterial**. COMSOL Multiphysics created this group when you performed the export from the Reaction Engineering Lab. Note how all the relevant edit fields of the subdomain setting are automatically filled in.
- 6 Click **OK**.
- 7 Choose **Multiphysics>2 Diffusion (chdi2)**.
- 8 Choose **Physics>Subdomain Settings**.
- 9 From the **Subdomain selection** list, select **2**, and then clear the **Active in this domain** check box.
- 10 From the **Subdomain selection** list, select **1**.
- 11 From the **Group** list, select **nerve**.
- 12 From the **Subdomain selection** list, select **3**.
- 13 From the **Group** list, select **fluid**.
- 14 Click **OK**.

Boundary Conditions

- 1 Choose **Multiphysics>1 Diffusion (chdi)**.
- 2 Choose **Physics>Boundary Settings**.
- 3 Go to the **Boundary Selection** list and select **4**, **7**, and **9** by Ctrl-clicking the entries.
- 4 Couple the species concentration variables of the biomaterial to the surroundings. For each species in the table, find the **Boundary condition** list and select **Concentration**. Then type the entries from the following table:

BOUNDARY	c_d	c_p	c_pd	c_e
4, 7, 9	c_D	c_P	c_PD	c_E

- 5 Leave the remaining boundary conditions at their default setting **Insulation/Symmetry**.
- 6 Click **OK**.
- 7 Choose **Multiphysics>2 Diffusion (chdi2)**.
- 8 Choose **Physics>Boundary Settings**.

- 9 Couple the species-concentration variables of the surroundings to the biomaterial.
For each species in the table, find the **Boundary condition** list and select **Concentration**. Then type the entries from the following table:

BOUNDARY	c_D	c_P	c_PD	c_E
4, 7, 9	c_d	c_p	c_pd	c_e

- 10 Leave all the other boundary conditions at their default setting **Insulation/symmetry**.
- 11 Click **OK**.

OPTIONS AND SETTINGS

- 1 Define the following expressions by choosing **Options>Expressions>Subdomain Expressions** and entering the settings in the table:

NAME	SUBDOMAINS 1, 3	SUBDOMAIN 2
c_peptide	c_P	c_p
c_drug	c_D	c_d
c_peptidedrug	c_PD	c_pd
c_enzyme	c_E	c_e

- 2 Click **OK**.

MESH GENERATION

- 1 Choose **Mesh>Free Mesh Parameters**.
- 2 Click the **Boundary** tab, go to the **Boundary selection** list, and select **4, 6, 7, and 9**.
Type $1e-4$ in the **Maximum element size** edit field.
- 3 Click **OK**.

COMPUTING THE SOLUTION

- 1 Click the **Solver Parameters** button on the Main toolbar.
- 2 In the **Times** edit field, type $0:600:7200$.
- 3 In the **Relative tolerance** edit field, type $1e-5$.
- 4 In the **Absolute tolerance** edit field, type $1e-6$.
- 5 Click **OK**.
- 6 Click the **Solve** button.

POSTPROCESSING AND VISUALIZATION

- 1 From the **Postprocessing** menu open the **Plot Parameters** dialog box.

- 2 On the **Surface Data** page, find the **Expression** edit field and type `c_drug`.
- 3 Click **OK**.
- 4 To create Figure 4-8, first go to the **Postprocessing** menu and open the **Cross-Section Plot Parameters** dialog box.
- 5 Go to the **General** page. In the **Solutions to use** area, select output times between 0 and 3600 by clicking **0** and then Shift-clicking **3600**.
- 6 Click the **Line/Extrusion** tab.
- 7 In the **y-axis data** area, find the **Expression** edit field and type `c_drug+c_peptidedrug`.
- 8 Go to the **Cross-section line data** area and enter the following values:

EDIT FIELD	ENTRY
x0	0
y0	3e-3
x1	5e-3
y1	3e-3

- 9 Click **Apply**.
- 10 To create Figure 4-9, return to the **Cross-section Plot Parameters** dialog box.
- 11 On the **General** page, go to the **Solutions to use** area and select all the entries by pressing Ctrl+A and clicking the output list.
- 12 In the **Expression** edit field, on the **Line/Extrusion** page, type `c_mp+c_mpd`.
- 13 Click **OK**.

Enzyme Inhibition Kinetics

Introduction

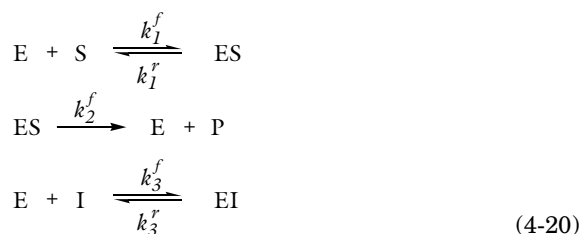
Enzymatic reactions often involve multiple coupled reaction steps in which many intermediary species take part. The concentrations of the intermediates may be very low, making them hard to isolate and quantify. It is often more practical to investigate the depletion of substrate or the accumulation of product under a series of different reaction conditions.

This example illustrates how you can perform parameter estimation making use of data from multiple experimental runs. In this case, the data consists of concentration transients of the reaction product, measured at different initial concentrations of reactant.

Model Description

Enzymes act as biological catalysts, efficiently and selectively transforming substrate into product. Factors like temperature and pH typically affect the enzyme reaction rates. Furthermore, the overall efficiency of enzymatic systems may also be affected by undesired side reactions where the enzymes form inactive complexes with molecules other than the substrate. Inhibition effects can be both beneficial and detrimental, which makes it relevant to study the mechanisms of enzyme reactions in detail.

In competitive inhibition, the substrate and inhibitor compete for the same active site on the enzyme. The corresponding kinetics can be described by the following reaction set:



In the main reaction sequence, the enzyme (E) and substrate (S) first form a complex (ES), which then produces the product (P). As a side reaction, the enzyme can also react with an inhibitor (I) forming the inactive complex (EI).

In an effort to evaluate kinetic parameters in the reaction network, experiments were set up to monitor concentration changes as functions of time. Rather than monitoring all species during a single experiment, the concentration transients of P were measured while varying the amount of inhibitor present in each run. The initial conditions of the experiments are summarized in the table below:

EXPERIMENT #	c_{0S} ($\mu\text{mol/L}$)	c_{0E} ($\mu\text{mol/L}$)	c_{0I} ($\mu\text{mol/L}$)
1	25	0.004	0
2	25	0.004	0.005
3	25	0.004	0.01
4	25	0.004	0.02

The corresponding experimental results are illustrated in Figure 4-10, where the data sets have been read into the Reaction Engineering Lab.

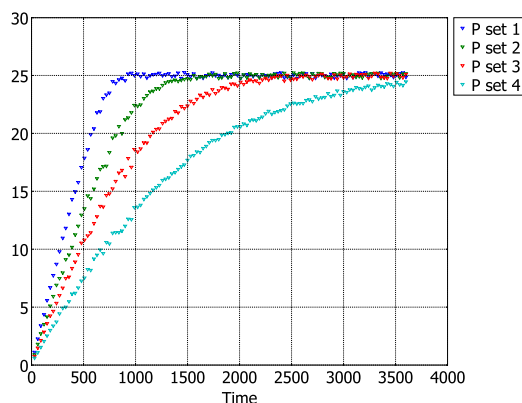


Figure 4-10: Four sets of data points representing the concentration of P ($\mu\text{mol/L}$) as function of time (s).

In this example it is assumed that the rate constants for the formation and decomposition of the ES complex are known from previous experiments; $k_1^f = 100 \mu\text{mol}/(\text{L s})$ and $k_1^r = 180 \text{ l/s}$. Furthermore, it is reasonable to assume that the rate constant describing the ES formation is similar to that of EI formation.

The parameter estimation will thus evaluate the rate constant of the product forming step, k_2^f , and the rate constant for the decomposition of EI, k_3^r .

Results

The parameter estimation produces the following results for the rate constants:

RATE CONSTANT	VALUE	LOWER LIMIT	UPPER LIMIT
kf_2	10.16	10.11	10.22
kr_3	9.80e-2	9.69e-2	9.90e-2

Figure 4-11 shows the experimental data along with the simulated results, using the rate constants found from parameter estimation.

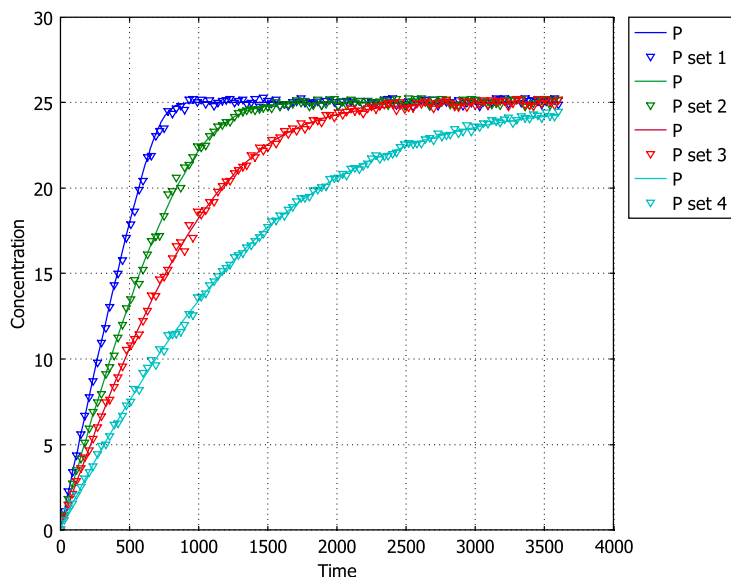


Figure 4-11: Four sets of data points representing the concentration of P ($\mu\text{mol/L}$) as function of time (s), and the corresponding simulation results.

Clearly, there is good agreement between theory and experiments. This indicates that the reaction mechanism describing the competitive inhibition (Equation 4-20) is indeed a good representation of what occurs in reality. Furthermore, the assumption that rate constant describing the formation of ES is equal to that of EI formation also appears valid.

Model Library path: Biochemistry/enzyme_inhibition

Modeling Using the COMSOL Reaction Engineering Lab

MODEL NAVIGATOR

- 1 Start the **COMSOL Reaction Engineering Lab** by double-clicking its desktop icon.
- 2 In the **Model Navigator** click the **New** button.

REACTIONS INTERFACE

- 1 From the **Model** menu, select **Reaction Settings**.
- 2 Create three entries in the **Reaction selection** list by clicking the **New** button three times.
- 3 Enter the reaction formulas in the table below by first selecting the appropriate row in the **Reaction selection** list and then typing the text in the **Formula** edit field.

REACTION ID #	REACTION FORMULA
1	$E + S \rightleftharpoons ES$
2	$ES \Rightarrow P + E$
3	$E + I \rightleftharpoons EI$

Note how Reaction Engineering Lab automatically generates the corresponding kinetic expressions and displays them in the **Reaction rate** edit field.

- 4 Enter the following values for the **Forward rate constant** and the **Reverse rate constant** by first selecting the appropriate row in the **Reaction selection** list and then typing the corresponding numbers in the **k^f** and **k^r** edit fields:

REACTION ID #	k ^f	k ^r
1	100	180
2	1	
3	100	1e-2

The values just entered for the rate constants serve as starting guesses for the parameter estimation. You can also supply starting guesses in the **Parameter Estimation Settings** dialog box.

SPECIES INTERFACE

- 1 While still in the **Reaction Settings** dialog box, click the **Species** tab.
- 2 On the **General** page, enter the following initial concentrations, one by one, in the **c₀** edit field after first having selected the appropriate entry in the **Species selection** list:

SPECIES NAME	c ₀
E	0.004
S	25
ES	0
P	0
I	0
EI	0

- 3 Click **Close**.

Move on to load experimental data into the software and set up the parameter estimation problem.

- 1 Choose **Estimation>Parameter Estimation Settings**.
- 2 Go to the **Advanced** page and select the **Specify initial state values for data sets** check box.

With this setting you activate the **Data/Init** page, where you specify which initial concentrations that apply to each individual data set.

- 3 Return to the **Data** page and click the **Import From File** button.
- 4 Browse to the text file `enzyme_inhibition_p_set1.txt` and click **Import**.
- 5 Similarly import the files `enzyme_inhibition_p_set2.txt`, `enzyme_inhibition_p_set3.txt`, and `enzyme_inhibition_p_set4.txt`.
- 6 Select `enzyme_inhibition_p_set1.txt` from the **Data set selection** list, and then **P set 1** from the **Data selection** list.
- 7 Select **P** from the **Predefined quantities** list.

With this procedure you have selected a particular data set and associated the data found in the column “P set 1” of the file with the corresponding variable name of the model, **P**.

- 8 Go to the **Init** page and select **Initial concentration I** in the **Variable selection** list.

- 9 Click the **Specify value** option button and type 0 in the corresponding edit field.
With these steps you tell the software that the initial concentration of the inhibitor (I) is 0 for this particular data set.
- 10 Proceed in the same manner to associate measured variables with model variables, and specifying the initial inhibitor concentration relevant for data set:

DATA SET	PREDEFINED QUANTITY	INITIAL CONCENTRATION I
enzyme_inhibition_p_set1.txt	P	0
enzyme_inhibition_p_set2.txt	P	5e - 3
enzyme_inhibition_p_set3.txt	P	10e - 3
enzyme_inhibition_p_set4.txt	P	20e - 3

- 11 Click the **Parameters** page.
- 12 From the **Predefined parameters** list, select **kf_2 (Forward rate constant 2)** and then click the **Add** button (>).
- 13 Repeat the above step for the parameter **kr_3 (Reverse rate constant 3)**.
Select **kf_2** and then **kr_3** from the **Parameters to estimate** list. Note that the **Use value from model** is selected by default. This indicates that the initial guesses of the parameters are the values entered in rate constant edit fields in the **Reaction Settings** dialog box.
- 14 Click **OK** to close the **Parameter Estimation Settings** dialog box.

COMPUTING THE SOLUTION

- 1 Click the **Estimate Parameters** button on the Main toolbar.
You find the estimated values of the rate constants **kf_2** and **kr_3** and their confidence limits displayed in the **Progress - Log** window. If the **Progress - Log** window is not open, access it by following the steps below:
- 2 Select the menu item **Estimation>View Log**.
- 3 Click the **Log** page.
You may have to scroll in the log to locate the summary report of the parameter estimation calculations. Selecting the **Close automatically** check box closes the **Progress - Log** window after each simulation.

Note that once the parameter estimation is finished, the reaction model is simulated automatically, using the rate constants just evaluated. You can turn off the automatic simulation feature on the **Advanced** page in the **Parameter Estimation Settings** dialog

box. Here, you can also select if you want automatic update of the evaluated parameters to the reaction model or not.

POSTPROCESSING AND VISUALIZATION

- 1 Choose **Postprocessing>Plot Parameters**.
- 2 Click the << button.
- 3 Go to the **Predefined quantities** list and select **P**.
- 4 Click the > button to add the entry to the **Quantities to plot** list.
- 5 Click **OK**.

The model results show the concentration of the product P evaluated when the initial concentration of the inhibitor is 0. To check that simulated results also align with the remaining data sets, follow the steps below.

SPECIES INTERFACE

- 1 From the **Model** menu, select **Reaction Settings**.
- 2 Click the **Species** tab.
- 3 On the **General** page select **I** from the **Species selection** list, and type 5e-3 in the **c₀** edit field.
- 4 Click **Close**.

COMPUTING THE SOLUTION

- 1 Click the **Solve** button on the Main Toolbar.

Repeat the above steps to check the simulations for initial concentrations 0.01 and 0.02.

Ozone Combustion

Introduction

This 1D example illustrates the detailed modeling of a premixed, laminar, steady-state flame where ozone undergoes combustion to form oxygen. Here seven reversible, elementary reactions describe the chemical degradation of ozone. The limited size of the reaction set makes this a good test case for combustion modeling (Ref. 1). The model couples mass, energy, and continuity equations describing the flame through dependencies on the temperature, pressure, and composition of the reacting flow. These relationships are given by expressions for thermodynamic and transport properties, which are provided at the level of detail commonly used by the combustion community.

It is well known that a flame has a limited range of operating conditions. If these conditions are not maintained, the flame does not remain stationary but instead can oscillate or fade. The technical question this model seeks to answer is this: How does the velocity of the inlet gas affect the flame in general and the chemistry in particular?

Model Definition

The modeling domain is in one dimension, 0.5 mm in length.

Assume pressure is constant at 101.3 kPa. At the inlet, a reacting gas mixture of 50% ozone and 50% oxygen (by weight) is held at 1000 K.

This example solves the stationary problem using three application modes:

- Maxwell-Stefan Diffusion and Convection to describe the mass balances
- Convection and Conduction to describe the overall energy balance
- PDE, General Form to describe the continuity equation

The mass balance per species i is described in the Maxwell-Stefan Diffusion and Convection application mode by

$$\nabla \cdot (\mathbf{j}_i + \rho \omega_i \mathbf{u}) = R_i \quad (4-21)$$

where ρ is the density (kg/m^3), w_i denotes the species mass fraction, \mathbf{u} equals the velocity vector (m/s), and R_i is the source term per species due to the chemical reaction ($\text{kg}/(\text{m}^3 \cdot \text{s})$). The \mathbf{j}_i diffusive mass flux of species i , is given by

$$\mathbf{j}_i = -D_i^T \nabla \ln T - \rho_i \sum_k \tilde{D}_{ik} \mathbf{d}_k \quad (4-22)$$

In this equation, the first term refers to the thermal diffusivity, which this example ignores. The components of the Fickian diffusivity matrix, D_{ik} (m^2/s), are calculated from the corresponding set of binary diffusion coefficients, which are calculated from kinetic gas theory in this way:

$$D_{AB} = 2.695 \cdot 10^{-3} \cdot \frac{\sqrt{T^3(M_A + M_B)/(2 \cdot 10^3 M_A M_B)}}{p \sigma_A \sigma_B \Omega_D} \quad (4-23)$$

Here D_{AB} is the binary diffusion coefficient (m^2/s), M denotes the molecular weight (kg/mol), T represents the temperature (K), p gives the pressure (Pa), σ is the characteristic length (\AA) of the Lennard-Jones/Stockmayer potential, and Ω_D is the collision integral.

The Convection and Conduction application mode describes the energy balance according to the equation

$$\nabla \cdot (-k \nabla T + \rho C_p T \mathbf{u}) = Q \quad (4-24)$$

where C_p is the fluid's heat capacity ($\text{J}/(\text{kg} \cdot \text{K})$) evaluated as the weight fraction average of the fluid components:

$$C_p = \sum_i w_i C_{p,i} \quad (4-25)$$

The model then calculates the heat capacity of the individual components from thermodynamic polynomials in the NASA format:

$$C_p = \frac{R_g}{M} (a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4) \quad (4-26)$$

where R_g is the ideal gas constant ($\text{J}/(\text{mol} \cdot \text{K})$), M_i equals the molar mass (kg/mol) of component i , and a_1 to a_5 are constants. Similarly, the fluid thermal conductivity, k ($\text{W}/(\text{m} \cdot \text{K})$), depends on temperature and fluid composition as

$$k = \frac{1}{2} \left[\sum_i x_i k_i + \left(\sum_i \frac{x_i}{k_i} \right)^{-1} \right] \quad (4-27)$$

where x_i is the mole fraction of species i . The thermal conductivity of the individual species is given by the Stiel-Thodos equation:

$$k = \eta \left(1.15 C_p + 0.88 \frac{R_g}{M} \right) \quad (4-28)$$

In Equation 4-28, the heat capacity C_p comes from Equation 4-26, and you evaluate the dynamic viscosity η (Ns/m²) using the following expression from kinetic gas theory:

$$\eta_i = 2.669 \cdot 10^{-6} \frac{\sqrt{T(M_i \cdot 10^3)}}{\sigma_i^2 \Omega_v} \quad (4-29)$$

Here, Ω_v denotes the collision integral.

In Equation 4-24, Q is the heat source (J/(m³·s)) due to a chemical reaction and is defined as

$$Q = \sum_j r_j H_j \quad (4-30)$$

where the reaction rates, r_j , come from Equation 4-47 discussed later. The heats of reaction, H_j (J/kg), are calculated as

$$H_j = - \sum_i \nu_{ij} h_i \quad (4-31)$$

where ν_{ij} is the stoichiometric coefficient of species i in reaction j , defined as being positive for reactants and negative for products. The enthalpy of each species is related to temperature by

$$h_i = \frac{R_g}{M_i} \left(a_{1i} T + \frac{a_{2i}}{2} T^2 + \frac{a_{3i}}{3} T^3 + \frac{a_{4i}}{4} T^4 + \frac{a_{5i}}{5} T^5 + a_{6i} \right) \quad (4-32)$$

This example models the overall mass conservation (continuity equation) using a **PDE, General Form** application mode

$$\nabla \cdot (\rho \mathbf{u}) = 0 \quad (4-33)$$

where ρ is the fluid density (kg/m³) expressed using the ideal gas law:

$$\rho = \frac{p}{R_g T} \sum_i x_i M_i \quad (4-34)$$

The boundary conditions imposed for the Maxwell-Stefan diffusion and convection are

$$w_i = w_{0,i} \quad \text{inlet} \quad (4-35)$$

$$\mathbf{n} \cdot \mathbf{j} = 0 \quad \text{outlet} \quad (4-36)$$

where \mathbf{j} is the diffusive mass flux. The boundary conditions for the convection/conduction application mode are

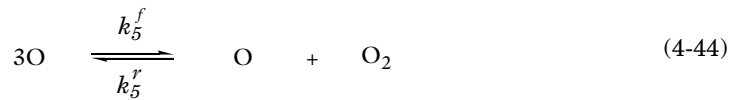
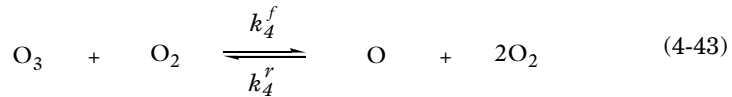
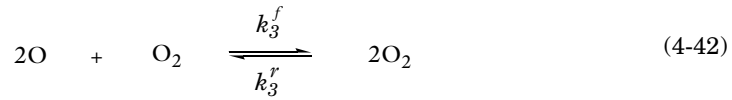
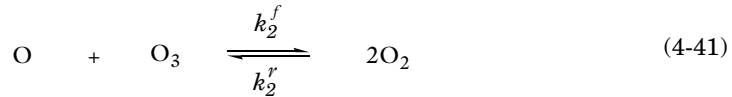
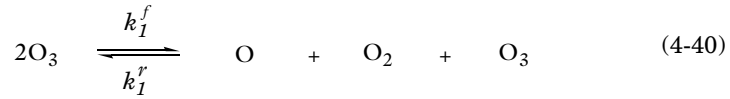
$$T = T_0 \quad \text{inlet} \quad (4-37)$$

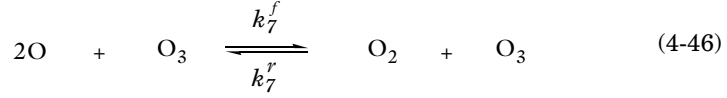
$$\mathbf{n} \cdot (-k \nabla T) = 0 \quad \text{outlet} \quad (4-38)$$

For the continuity equation, the gas velocity is specified at the inlet as

$$u = u_0 \quad \text{inlet} \quad (4-39)$$

The following set of elementary reactions describe the chemistry of ozone combustion:





The rate (mol/(m³·s)) of reaction j is given by

$$r_j = k_j^f \prod_{i \in \text{react}} c_i^{-\nu_{ij}} - k_j^r \prod_{i \in \text{prod}} c_i^{\nu_{ij}} \quad (4-47)$$

Here, k_j^f and k_j^r denote the forward and reverse rate constants, respectively. The concentration of species i is denoted c_i (mol/m³). The stoichiometric coefficients are denoted ν_{ij} . The temperature dependence of the rate constants is given by the Arrhenius expression

$$k_j = AT^n \exp\left(-\frac{E}{R_g T}\right) \quad (4-48)$$

where A is the frequency factor, n represents the temperature exponent, and E equals the activation energy (J/mol).

This example first solves the model for fixed inlet conditions with a velocity of 1 m/s, a temperature of 500 K, and a gas mixture of 50% ozone and 50% oxygen using the Stationary Nonlinear solver. Then it solves the model for a sweep of values of the inlet velocity using the Parametric solver.

Results

Figure 4-12 shows the evolution of the gas composition along the length of the flame. The reaction paths described by Equation 4-40 to Equation 4-46 lead to ozone decomposition into oxygen.

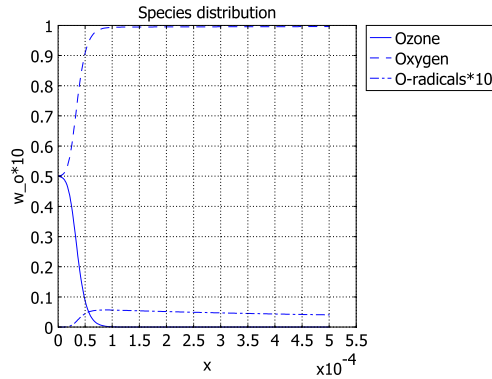


Figure 4-12: Species distribution (weight fraction) in the reacting flow.

The results indicate that the reaction takes place in the first 100 μm of the flame. The figure also illustrates that the weight fraction of oxygen radicals is relatively small. The results show values in the range of weight fraction near 0.5%. Furthermore, the radical concentration seems to remain at that level even at the outlet, suggesting a slow radical termination reaction.

Figure 4-13 shows the thermal effects at an inlet velocity of 1 m/s.

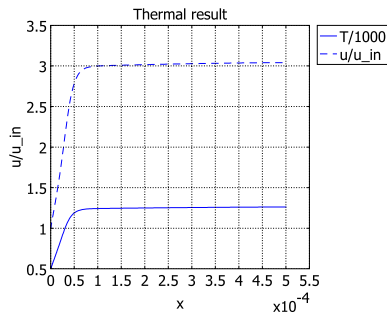


Figure 4-13: Thermal effects in terms of temperature and velocity profile.

In total, the combustion reactions are exothermic, resulting in a rapid release of energy and increase of temperature at the reaction zone. This increase in temperature leads to a higher gas velocity due to a rapid density decrease.

The model explores the influence of the inlet velocity on the results. This case varies the inlet velocity from 3.0 to 0.01 m/s. Figure 4-14 shows how this velocity variation affects the concentration profile of ozone, and it indicates that the reaction zone becomes very narrow as the velocity increases. Furthermore, the geometrical offset from the inlet to where the reaction starts increases slightly at the highest velocities.

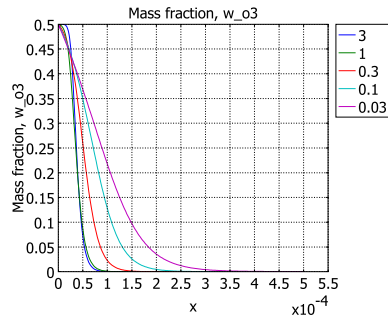


Figure 4-14: Ozone weight fraction profiles for various inlet velocities.

The inlet velocity also strongly affects the flame's temperature as seen in Figure 4-15.

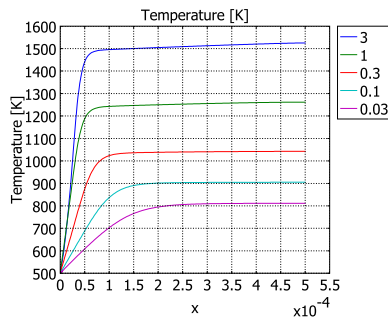


Figure 4-15: Temperature profiles for various inlet velocities.

As a consequence of the increasing temperature, the velocity is also affected. Figure 4-16 shows the gas velocity in the flame in relation to the inlet velocity, that is, the relative velocity.

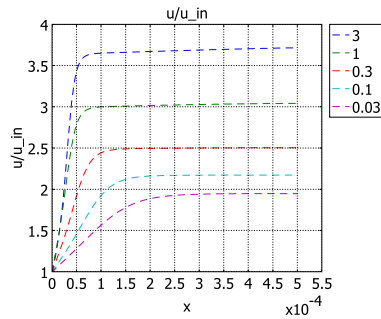


Figure 4-16: Relative velocity profiles at various inlet velocities.

In conclusion, this example shows the setup and solution of a combustion problem making use of the Reaction Engineering Lab together with the Chemical Engineering Module. The Reaction Engineering Lab automatically formulates a kinetic scheme involving seven reversible ozone reactions when you enter the corresponding reaction formulas into the user interface. The accurate modeling of the decomposition process furthermore made use of the predefined expression for thermodynamics and transport properties available in the Reaction Engineering Lab.

Reference

1. J.M. Heimerl and T.P. Coffee, *Combustion and Flame*, vol. 39, p. 301, 1980.

Model Library path: Combustion/ozone_combustion

The following path shows the location of the COMSOL Multiphysics model:

Model Library path:

Reaction_Engineering_Lab/Combustion/ozone_combustion

MODEL NAVIGATOR

- 1 Start the Reaction Engineering Lab.
- 2 Click **New** in the **Model Navigator**.

SETTINGS AND PARAMETERS

- 1 Choose **Model>Model Settings**.
- 2 Select the **Calculate thermodynamic properties** check box.
- 3 Select the **Calculate species transport properties** check box.
- 4 Type 900 in the **T** edit field, then click **Close**.

REACTIONS INTERFACE

- 1 Choose **Model>Reaction Settings**.
- 2 Create seven entries in the **Reaction selection** list by clicking the **New** button seven times.
- 3 Enter the following reaction formulas by first selecting the appropriate row in the **Reaction selection** list and then typing the text in the **Formula** edit field. Note how the Reaction Engineering Lab automatically generates reaction rate expressions and presents them in the **r** edit field.

REACTION ID #	REACTION FORMULA
1	$2\text{O}_3 \rightleftharpoons \text{O}_3 + \text{O}_2 + \text{O}$
2	$\text{O} + \text{O}_3 \rightleftharpoons 2\text{O}_2$
3	$2\text{O} + \text{O}_2 \rightleftharpoons 2\text{O}_2$
4	$\text{O}_3 + \text{O}_2 \rightleftharpoons \text{O} + 2\text{O}_2$
5	$3\text{O} \rightleftharpoons \text{O} + \text{O}_2$
6	$\text{O}_3 + \text{O} \rightleftharpoons 2\text{O} + \text{O}_2$
7	$2\text{O} + \text{O}_3 \rightleftharpoons \text{O}_2 + \text{O}_3$

- 4 On the **Kinetics** page, specify the Arrhenius parameters for the forward and reverse rate constants according to the table below. To do so, first select the appropriate row

in the **Reaction selection** list, then select the **Use Arrhenius expressions** check box, and finally type the numbers in the corresponding edit field in the **Arrhenius** area:

REACTION ID #	A		n		E	
	forward	reverse	forward	reverse	forward	reverse
1	4.31e8	1.2e1	0	0	92.8e3	-8.11e3
2	1.14e7	1.19e7	0	0	19.1e3	420.7e3
3	1.38e6	2.75e13	-1	-1	1.42e3	496.6e3

- 5 The rate constants of reactions 4 through 7 are related to rate constants of reactions 1 through 3. In the k^f and k^r edit fields, replace the predefined expressions with the following relations:

REACTION ID #	k^f	k^r
4	$0.44 * k_{f_1}$	$0.44 * k_{r_1}$
5	$3.6 * k_{f_3}$	$3.6 * k_{r_3}$
6	$0.44 * k_{f_1}$	$0.44 * k_{r_1}$
7	k_{f_3}	k_{r_3}

SPECIES INTERFACE

- Click the **Species** tab.
- Check that the **Species selection** list has the following three entries: **o3**, **o2**, and **o**.
- On the **General** page enter the following values for the **Molecular weight** in the **M** edit field and also enter values for the **Initial concentration** in the **c₀** edit field after selecting the appropriate entry in the **Species selection** list:

SPECIES NAME	M	c ₀
o3	48e-3	16.25
o2	32e-3	24.37
o	16e-3	0

- Click the **Thermo** tab.
- Select all the species in the **Species selection** list by pressing Ctrl+A and clicking anywhere in the list. Enter the numbers 3e2, 1e3, and 6e3 in the edit fields for the **lower**, **midpoint**, and **upper** temperature interval, **T_{int}**.
- Select one entry at a time from the **Species selection** list and type the following vectors of polynomial coefficients in the edit fields for **a_{low,k}** and **a_{high,k}**:

COEFFICIENT	O3	O2	O
$a_{low,1}$	0.2466e1	0.3625e1	0.2955e1
$a_{low,2}$	0.9170e-2	-0.1878e-2	-0.1706e-2
$a_{low,3}$	-0.4969e-5	0.7055e-5	0.2592e-5
$a_{low,4}$	-0.2063e-8	-0.6763e-8	-0.1783e-8
$a_{low,5}$	0.2001e-11	0.2155e-11	0.4570e-12
$a_{low,6}$	0.1605e5	-0.1047e4	0.2914e5
$a_{high,1}$	0.5466e1	0.3621e1	0.2535e1
$a_{high,2}$	0.1732e-2	0.7361e-3	-0.1437e-4
$a_{high,3}$	-0.7220e-6	-0.1965e-6	-0.1136e-7
$a_{high,4}$	0.1372e-9	0.3620e-10	0.6600e-11
$a_{high,5}$	-0.9623e-14	-0.2894e-14	-0.6118e-15
$a_{high,6}$	0.1521e5	-0.1201e4	0.2923e5

Note that only six out of seven edit fields are used. This is fine because the NASA polynomial format uses the seventh edit field only to calculate the species entropy, an expression this model does not use.

Reaction Settings

Reactions Species

Species selection

- ☒ O3
- ☒ O2
- ☒ O

Formula: O3 Type: [dropdown]

General Feed Stream Thermo Transport

Thermodynamic parameters

Quantity	Value/Expression	Unit	Description
T_{int}	lower: 3e2, midpoint: 1e3, upper: 6e3	K	Temperature interval limits
$a_{low,k}$	0.2466e1 0.9170e-2 -0.4969e-5		Polynomial coefficients
$a_{hi,k}$	0 0 0 0 0 0		Polynomial coefficients

Thermodynamic expressions

Quantity	Value/Expression	Unit	Description
s	$Rg^*(T \leq T_{lo_o3}) * a_{lo1_o3} \log()$	J/(mol·K)	Molar entropy
h	$Rg^*(T \leq T_{lo_o3}) * T_{lo_o3} * a_{lo1_o3}$	J/mol	Molar enthalpy
C_p	$Rg^*(T \leq T_{lo_o3}) * (a_{lo1_o3} + a_{lo2_o3})$	J/(mol·K)	Heat capacity at constant pressure

New Delete Reset

Close Help

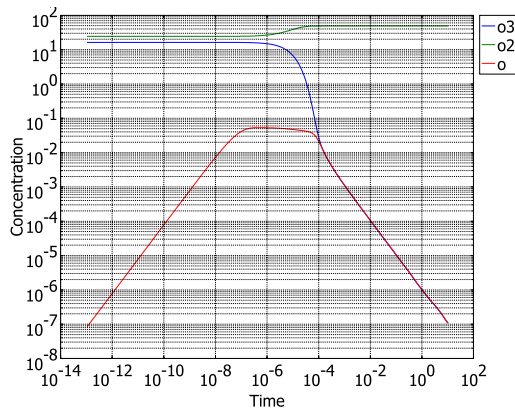
- 7 Click the **Transport** tab.
- 8 Enter the following interaction potential parameters into the ϵ/k_b and σ edit fields after selecting the appropriate entry in the **Species selection** list:

SPECIES NAME	σ	ϵ/k_b
o3	4.69	39.4
o2	3.372	128.7
o	2.947	127.2

- 9 Click **Close**.

COMPUTING THE SOLUTION

- 1 Click the **Solver Parameters** button on the Main toolbar.
- 2 In the **Times** edit field, type 10. Click **OK**.
- 3 Click the **Solve Problem** button (=).
- 4 To get a good overview of the results, click both the **X log** and the **Y log** buttons on the Main toolbar to switch to a log-log plot.
- 5 Go to the figure window and click the **Edit Plot** button to open the **Edit Plot** dialog box. Open the **Grid** page and clear the **Show grid** check box. You should now get the following plot:



EXPORT SETTINGS

- 1 From the **File** menu, select **Export>Model to COMSOL Multiphysics**.

- 2 Select **ID** from the **Space dimension** list, then click **OK**.
This step launches COMSOL Multiphysics and opens the **Export to COMSOL Multiphysics** dialog box.
- 3 In the **Export mass balance** area, select **Maxwell-Stefan Diffusion and Convection: New** from the **Application mode** list.
- 4 In the **Group name** edit field, type **mass**.
- 5 In the **Export energy balance** area, select **Convection and Conduction: New** from the **Application mode** list.
- 6 In the **Group name** edit field, type **energy**.
- 7 Click **Export**.

Modeling Using COMSOL Multiphysics

MODEL NAVIGATOR

- 1 From the **Multiphysics** menu, select **Model Navigator**.
- 2 Verify that the model contains the **Maxwell-Stefan Diffusion and Convection (chms)** and the **Convection and Conduction (chcc)** application modes as a result of the export from the Reaction Engineering Lab.
- 3 From the list of application modes, select **COMSOL Multiphysics>PDE Modes>PDE, General Form**.
- 4 Click **Add**.
- 5 Click **OK**.

OPTIONS AND SETTINGS

- 1 Define the following constants by choosing **Options>Constants** and typing them in:

NAME	EXPRESSION	DESCRIPTION
w_o3_in	0.5	Inlet weight fraction o3
w_o2_in	0.5	Inlet weight fraction o2
T_in	500	Inlet temperature
u_in	1	Inlet gas velocity

- 2 Click **OK**.

GEOMETRY MODELING

- 1 Choose **Draw>Specify Objects>Line**.

- 2 In the **x** edit field, type 0.5e-4, and then click **OK**.
- 3 Click the **Zoom Extents** button on the Main toolbar.

PHYSICS SETTINGS

Subdomain Settings

- 1 Choose **Multiphysics>Maxwell-Stefan Conduction and Convection (chms)**.
- 2 Choose **Physics>Subdomain Settings**.
- 3 In the **Subdomain selection** list on the **Subdomains** page, select **1**.
- 4 Still on the **Subdomains** page, select **mass** from the **Group** list.
Note how all the relevant edit fields are filled in with the values exported from the Reaction Engineering Lab.
- 5 On the **General** page, type **u** in the **x-velocity** edit field.
- 6 On the **Init** page, type 0.05 in the **w_o3(t₀)** edit field and type 0.92 in the **w_o2(t₀)** edit field.
- 7 Click **OK**.
- 8 Choose **Multiphysics>Convection and Conduction (chcc)**.
- 9 Choose **Physics>Subdomain Settings**.
- 10 On the **Subdomains** page, select **energy** from the **Group** list.
This group setting was also created during the export from the Reaction Engineering Lab to COMSOL Multiphysics.
- 11 On the **Physics** page, type **u** in the **x-velocity** edit field.
- 12 On the **Init** page, type **T_in** in the **T(t₀)** edit field.
- 13 Click **OK**.
- 14 Choose **Multiphysics>PDE, General Form (g)**.
- 15 Choose **Physics>Subdomain Settings**.
- 16 On the **Coefficients** page, type the following data into the indicated edit fields:

PROPERTY	VALUE
Γ	0
F	$-(\rho_{rxn_chcc} * u + \text{diff}(\rho_{rxn_chcc}, x) * u)$
e_a	0
d_a	0

- 17 On the **Init** page, type **u_in** in the **u(t₀)** edit field.

18 Click **OK**.

Boundary Conditions

1 With the application mode **PDE, General Form (g)** still active, choose **Physics>Boundary Settings**.

2 Enter the boundary conditions according to the following table:

SETTINGS	BOUNDARY 1	BOUNDARY 2
Type	Dirichlet	Neumann
G	0	0
R	$u_{in} - u$	

3 Click **OK**.

4 Choose **Multiphysics>Maxwell-Stefan Diffusion and Convection (chms)**.

5 Choose **Physics>Boundary Settings**.

6 Enter the boundary conditions according to the following table:

SETTINGS	BOUNDARY 1	BOUNDARY 2
w_o3	Mass fraction, $w_{o30} = w_{o3_in}$	Convective Flux
w_o2	Mass fraction, $w_{o20} = w_{o2_in}$	Convective Flux

7 Click **OK**.

8 Choose **Multiphysics>Convection and Conduction (chcc)**.

9 Choose **Physics>Boundary Settings**.

10 Enter the boundary conditions according to the following table:

SETTINGS	BOUNDARY 1	BOUNDARY 2
Type	Temperature	Convective Flux
Value	T_{in}	

11 Click **OK**.

MESH GENERATION

1 Choose **Mesh>Free Mesh Parameters**.

2 On the **Global** page, type $0.5e-5$ in the **Maximum element size** edit field.

3 In the **Element growth rate** edit field, type 1.1 .

- 4 Click the **Boundary** tab, select Boundary 1, and type $1e-10$ in the **Maximum element size** edit field.
- 5 Click **Remesh** and then click **OK**.

COMPUTING THE FIRST SOLUTION

- 1 Choose **Solve>Solver Parameters**.
- 2 Select **Stationary** in the **Solver** list.
- 3 Click **OK**.
- 4 Solve the problem by clicking the **Solve** button (=) on the Main toolbar.

POSTPROCESSING THE FIRST SOLUTION

The following steps reproduce Figure 4-12:

- 1 Choose **Postprocessing>Domain Plot Parameters**.
- 2 On the **General** page, select the **Keep current plot** check box.
- 3 On the **Line/Extrusion** page, select Subdomain 1.
- 4 From the **Predefined quantities** list, select **Mass Fraction, w_o3 (chms)**.
- 5 Plot the first line by clicking **Apply**.
- 6 In the **Line/Extrusion** page, select **Mass Fraction, w_o2 (chms)** in the **Predefined quantities** list.
- 7 Click the **Line Settings** button. From the **Line color** list select **Color**, then click **OK**.
- 8 Plot the second line by clicking **Apply**.
- 9 On the **Line/Extrusion** page, type w_o*10 in the **Expression** edit field.
- 10 Click the **Line Settings** button. From the **Line color** list, select **Color**. Click the **Color** button, select green from the palette, and click **OK**.
- 11 Click **OK**.
- 12 Go to the figure window and click the **Edit Plot** button to open the **Edit Plot** dialog box.
- 13 Click on **Axes** in the list, then type **Species distribution** in the **Title** edit field. Also, type **Mass fractions** in the **y label** edit field.
- 14 Click the top **line(0)** object in the list. This corresponds to the line first plotted.
- 15 Select the **Show legend** check box and type **Ozone** in the **Legends** edit field.
- 16 Repeat the last two steps for the two remaining **line(0)** objects using the legend names **Oxygen** and **O-radicals*10**, respectively.

17 Click **OK** to finalize the plot.

Create Figure 4-13 with the following steps:

- 1 Choose **Postprocessing>Domain Plot Parameters**.
- 2 On the **General** page, select **New figure** from the **Plot in** list.
- 3 On the **Line/Extrusion** page, type $T/1000$ in the **Expression** edit field, then click **Apply**.
- 4 Still on the **Line/Extrusion** page, type u/u_{in} in the **Expression** edit field.
- 5 Click the **Line Settings** button. From the **Line color** list, select **Cycle**, then click **OK**.
- 6 Click **OK**.
- 7 In the figure window, click the **Edit Plot** toolbar button.
- 8 Click on **Axes** in the list and type **Thermal result** in the **Title** edit field. Also type u/u_{in} ; $T/1000$ in the **y label** edit field.
- 9 Click the top **line(0)** object in the list, click to select the **Show legend** check box, and type $T/1000$ in the **Legends** edit field.
- 10 Repeat the last step for the other **line(0)** object using the legend name u/u_{in} .
- 11 Click **OK** to finalize the plot.

COMPUTING THE PARAMETRIC SOLUTIONS

- 1 Choose **Solve>Solver Parameters**, then select **Parametric** in the **Solver** list.
- 2 Type u_{in} in the **Parameter name** edit field and $3 \quad 1 \quad 0.3 \quad 0.1 \quad 0.03$ in the **Parameter values** edit field.
- 3 On the **Advanced** page, click to clear the **Stop if error due to undefined operation** check box. Click **OK**.
- 4 Choose **Solve>Solver Manager**. In the **Initial value** area of the **Initial Value** page, select **Current solution**. Click **OK**.
- 5 Click the **Solve** button on the Main toolbar. The solution process takes a few minutes on a standard PC.

POSTPROCESSING THE PARAMETRIC SOLUTION

The following steps reproduce Figure 4-14:

- 1 Choose **Postprocessing>Domain Plot Parameters**.
- 2 On the **General** page, select **New figure** from the **Plot in** list.
- 3 On the **Line/Extrusion** page, select **Mass Fraction, w_{o3}** from the **Predefined quantities** list.

- 4 Click the **Line Settings** button, then select the **Legends** check box and click **OK**.
- 5 Generate the plot by clicking **OK**.

To reproduce Figure 4-15, repeat the steps above except this time select **Temperature (chcc)** from the **Predefined quantities** list.

Finally, to create Figure 4-16, repeat the steps above, but this time type u/u_{in} in the **Expression** edit field instead of selecting a variable from the list.

Diesel Filter

This example deals with a model of a filter system for a diesel engine. A porous membrane separates soot particles from exhaust gases passing through it, leading to the formation of a soot layer. Both catalytic and noncatalytic reactions retard the layer's build-up; carbon is oxidized to carbon monoxide and carbon dioxide, which both pass through the membrane.

Introduction

Diesel filters are used to remove particulate matter in diesel-engine exhaust gases. A filter system's efficiency and durability are closely related to the manner in which it removes soot deposits from the porous filter walls. For instance, one method is to remove the soot layer by means of noncatalytic reactions with oxygen. However, this scheme requires that the exhaust temperature increase above normal operating conditions. Another approach involves introducing cerium additives to the fuel. Cerium oxide species are subsequently present in the soot layer, acting as a catalyst in carbon-oxidation reactions. Under these conditions, it is possible to remove carbon deposits in the filter without increasing the exhaust temperature. The following model illustrates both of these working conditions.

Diesel filters are typically of a monolithic type with narrow channels running through a cylindrical structure. The silicon carbide filter under study is 15 cm long with a total of 2000 channels. Filter channels are open only at one end and are arranged in an alternating fashion in the monolith. The channels are separated by porous walls, as illustrated in Figure 4-17.

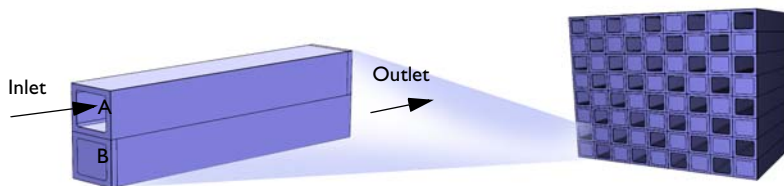


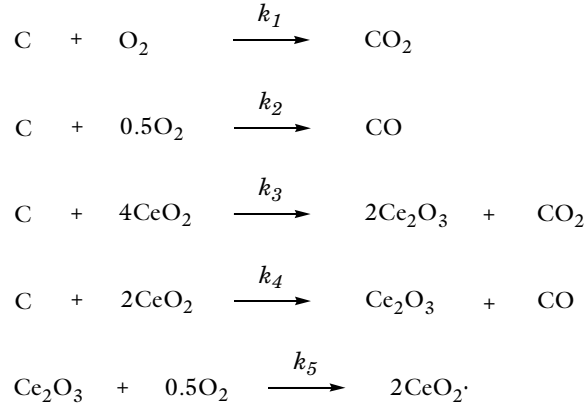
Figure 4-17: Front view of a channel section in a diesel filter. The A-channels are open while the B-channels are closed. Channels are separated by porous walls. A back view would show the opposite configuration. Gas therefore enters the filter through the A-channels and exits through the B-channels.

THE CHEMICAL REACTIONS AND THE 1D MODELS

Begin this example with an overview of the system chemistry.

The soot layer must be removed continuously or at intervals to keep the filter in working condition. Oxygen can react with carbon to form carbon monoxide and carbon dioxide. Further reaction pathways open when the diesel fuel is treated with additives containing cerium. The soot layer then contains cerium-oxide species that act as catalysts to oxidize the carbon, and oxygen regenerates the catalyst.

This model considers the following reactions taking place in the soot layer:



The reactions occur in the soot layer. The reaction rates ($\text{mol}/(\text{m}^3 \cdot \text{s})$) are given by

$$r_1 = k_1 c_{\text{O}_2}$$

$$r_2 = k_2 c_{\text{O}_2}$$

$$r_3 = k_3 x_{\text{CeO}_2}$$

$$r_4 = k_4 x_{\text{CeO}_2}$$

$$r_5 = k_5 x_{\text{Ce}_2\text{O}_3} c_{\text{O}_2}$$

where c_{O_2} is the molar concentration of oxygen (mol/m^3), while x_{CeO_2} and $x_{\text{Ce}_2\text{O}_3}$ are the molar fractions of the different cerium species.

The Reaction Engineering Lab automatically defines the material and energy balances for a perfectly mixed batch reactor.

An alternative way to define a steady-state model for a tubular reactor in the Reaction Engineering Lab is to use time, t , as the dependent variable. At steady state and at a given constant velocity, you can use the time variable to step in space.

For example, consider the material balance for an isothermal tubular reactor where you neglect transport by diffusion in the direction of the flow. You can then define a material balance according to

$$\frac{d}{dx}(c_i u) - R_i = 0$$

where u is the velocity and R_i includes all the reactions in which species i is involved. You can directly use the time t as the x coordinate, remembering that the time interval now represents the reactor length. Alternatively, substitute the relation $u = dx/dt$ in the previous equation to get an equation that truly depends on time. The second option implies that you travel with the flow along the length of the reactor during time stepping. Both cases only require an initial or inlet condition for the concentration.

It is advisable to follow a two-step strategy in the Reaction Engineering Lab to get a feeling for this system (the modeling steps are independent of each other):

- 1 Model a perfectly stirred tank reactor including the system kinetics; then export that Reaction Engineering Lab model to the Chemical Engineering Module in COMSOL Multiphysics to set up a time-dependent 2D model. In both the Reaction Engineering Lab and COMSOL Multiphysics, the model includes an energy balance but still assumes that nitrogen acts as a solvent.
- 2 The second model is only done in the Reaction Engineering Lab and involves the definition of a 1D tubular reactor for the system. This model can be isothermal assuming that nitrogen acts as a solvent.

The assumption that nitrogen is present in a dominating concentration is not completely acceptable for a high-fidelity model. However, as a first step you can be satisfied with a description that has the correct order of magnitude.

Now look at a material balance at a constant pressure and a constant temperature in one cell in the monolithic filter (here neglecting any pressure losses in the system). Assume you can put part of the filter into an experimental setup as shown in Figure 4-18 so that you can study one single cell and one single filter-unit. The exhaust gas enters Channel A and passes through a single filter wall to Channel B (note that a

repetitive cell would have a filter wall on all sides). Because not much happens in Channel B, you can restrict the 1D model system to treat just Channel A, the deposited particles, and the catalyst. Along the system boundaries, the filter is a distributed outlet (again see Figure 4-18). Because the pressure loss over the filter wall is comparably large, you can, furthermore, assume that the velocity across the wall along the length of the channel is constant. This implies that the velocity component along the channel decreases linearly from the inlet to the outlet.

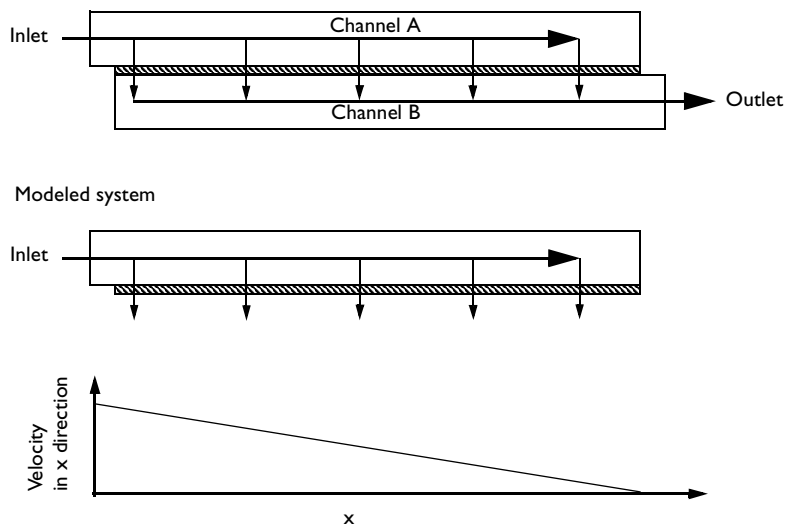


Figure 4-18: Cross section of the modeled system. The exhaust enters Channel A, goes through the filter wall, and exits through Channel B. Assume the velocity across the filter wall is constant along the x direction in the 1D model, while the velocity component along the length of the channel decreases linearly with the distance from the inlet.

A general material balance for a small section of Channel A of length Δx resembles the following equation for any species i :

$$(N_{i,x+\Delta x} - N_{i,x})A_{cs} + \Delta x c_i v_f - \Delta x A_{cs} R_i = 0 \quad (4-49)$$

Here N_i denotes the flux vector ($\text{mol}/(\text{m}^2 \cdot \text{s})$), A_{cs} equals the channel's cross-sectional surface (m^2), v_f represents the flow velocity across the filter (m/s), and R_i ($\text{mol}/(\text{m}^3 \cdot \text{s})$) is the reaction rate per unit volume of the channel, which includes all the reactions in which i takes part. The reaction is limited to the soot layer on the filter surface. Because the kinetic data is given per unit volume of soot, you must estimate the volume of soot per unit volume of the channel. Do so by assuming a given soot

layer thickness; the relationship between the soot-layer thickness and channel height then gives the volume of soot per unit volume of channel ($\delta_{\text{soot}}/\delta_{\text{channel}}$).

Dividing Equation 4-49 by the cross-sectional area A_{cs} and Δx as you let Δx approach zero results in the equation

$$\frac{dN_i}{dx} + c_i \frac{v_f}{A_{cs}} - R_i = 0.$$

Assuming that the transport of species in the x direction is dominated by convection gives

$$\frac{d(c_i u)}{dx} + c_i \frac{v_f}{A_{cs}} - R_i = 0 \quad (4-50)$$

where u is the flow velocity in the x direction (m/s). However, according to the assumption of a linearly decreasing flow along the channel, you can express u as

$$u = k_u x + u_0 \quad (4-51)$$

where k_u (1/s) denotes the proportionality constant (-1 times the inlet velocity divided by the channel length), and u_0 equals the inlet velocity. Equation 4-51 inserted into Equation 4-50 results in the following expression (after making use of the differentiation rule for products):

$$u \frac{dc_i}{dx} + k_u c_i + c_i \frac{v_f}{A_{cs}} - R_i = 0 \quad (4-52)$$

The Reaction Engineering Lab automatically calculates the R_i term from the reaction formulas. You can add the second and third terms manually as sources or sinks directly in the user interface.

THE 2D MODEL

This example removes a channel section from the monolith and places it into an experimental setup to study only a single filter unit with a single filter wall. Assuming that you use only a single filter wall and by thermally and mechanically insulating the

upper and vertical channel walls, you can treat the system with a 2D model as in the following figure:

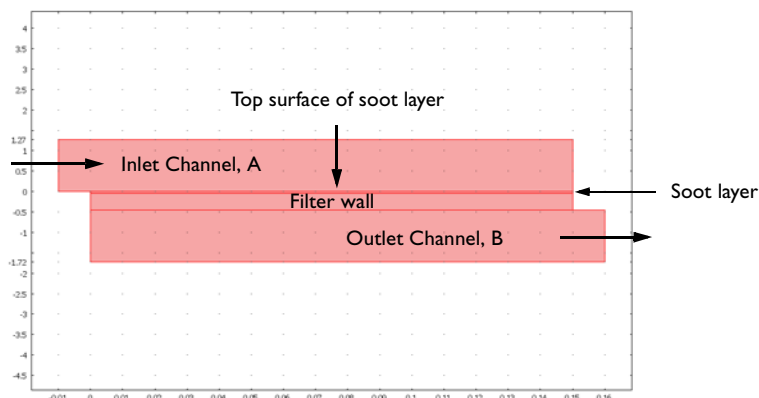


Figure 4-19: Modeled domain including four subdomains: the inlet Channel A, soot layer, filter wall, and outlet Channel B.

The model includes four distinct subdomains: the inlet Channel A, the soot layer on the surface of the filter wall, the filter wall, and the outlet Channel B.

The filter is 15 cm long, and the height of a single channel is 1.27 mm. The filter wall is 0.40 mm thick. Diesel exhaust gas enters the inlet channel, and the gas containing soot particles filters off through the porous SiC filter wall, thereby leaving a soot layer on top of this wall. The exhaust exits the filter through the outlet channel. This example model adds a short inlet-adapter zone and a corresponding outlet-adapter zone to make it easier to define stable boundary conditions. You must treat the top surface of the soot layer as a moving sub-boundary that grows and shrinks according to the amount of soot.

To solve this model, use four application modes in the Chemical Engineering Module:

- Weakly Compressible Navier-Stokes
- Darcy's Law
- Convection and Diffusion (material balance)
- Convection and Conduction (energy balance)

In addition, a Moving Mesh (ALE) application mode from COMSOL Multiphysics handles the moving top boundary of the soot layer.

The Weakly Compressible Navier-Stokes application mode is defined in both the inlet and outlet channels. The Darcy's Law application mode is defined in the soot layer and the filter wall. The Convection and Diffusion application mode is defined in all four subdomains as are the Convection and Conduction and the Moving Mesh ALE application modes.

There are three issues worth mentioning regarding the domain equations and boundary conditions used in the model implementation:

- The top surface of the soot layer represents an outer boundary for the Weakly Compressible Navier-Stokes application mode. At this boundary the velocity components (x and y) of this application mode are set equal to those of the Darcy's Law application mode. The same procedure is followed at the lower filter wall surface (the one facing the outlet channel). At the same boundaries, the Darcy's Law application mode boundary conditions state that the pressure should be equal to that of the Weakly Compressible Navier-Stokes Flow application mode.
- The Moving Mesh ALE application mode needs an expression for the mesh velocity at the top surface of the soot layer. This expression comes from the equation

$$v_y = \left(-\frac{\rho_{\text{part}}}{\rho_{\text{soot}}} \right) v - \frac{M_c \delta_{\text{sl}}}{\rho_{\text{soot}}} R_c$$

where v_y is the mesh velocity, v is the y -component of the flow velocity at the top surface of the soot layer, M_c equals the molar weight of carbon, R_c denotes the sum of all carbon-consuming reaction rates (averaged across the layer thickness), and δ_{sl} equals the soot layer's thickness.

- Note that the properties of the porous filter wall and soot layer are a combination of those of solids and fluids. For example, in the energy balance, the conduction term should include the conductivities of the solid and the fluid, while the convection term should contain only the properties of the fluid because the solid does not move. The accumulation (time-dependent) term should include a mixture of both properties in this way:

$$\rho_{\text{mix}} = \rho_{\text{solid}}(1 - \epsilon_{\text{solid}}) + \rho_{\text{gas}}\epsilon_{\text{solid}}$$

$$C_{p_{\text{mix}}} = C_{p_{\text{solid}}}(1 - \epsilon_{\text{solid}}) + C_{p_{\text{gas}}}\epsilon_{\text{solid}}$$

$$k_{\text{mix}} = k_{\text{solid}}(1 - \epsilon_{\text{solid}}) + k_{\text{gas}}\epsilon_{\text{solid}}$$

where ρ_{mix} is the mixture's density (kg/m^3), $C_{p,\text{mix}}$ is its heat capacity ($\text{J}/(\text{kg}\cdot\text{K})$), k_{mix} equals its thermal conductivity ($\text{W}/(\text{m}\cdot\text{K})$), and ϵ_{solid} the void fraction (porosity).

Results

THE CHEMICAL REACTIONS AND 1D MODELS

Start by looking at a 1D-model isothermal model, solved for in the Reaction Engineering Lab, describing a simplified tubular reactor model for Channel A, according to Equation 4-52. The following figures depict the species' concentration along the channel length at two different temperatures, one below “catalyzer ignition” temperature, and one above.

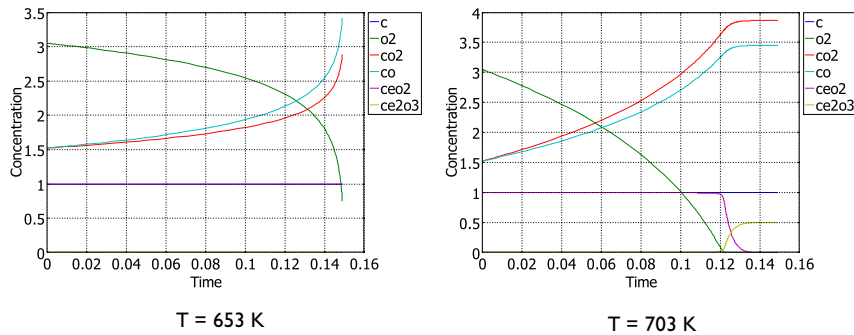


Figure 4-20: Composition along the length of the reactor for two operation temperatures, 653 K and 703 K.

An interesting effect arises at 703 K when the oxygen is depleted. As the temperature increases, the rate of oxidation increases until depletion of oxygen take place in the reactor. The rate of CeO_2 regeneration then decreases substantially and Ce_2O_3 becomes the dominating cerium species.

It is interesting to study the ratio of the non-catalyzed to the catalyzed reaction rates for the carbon monoxide and carbon dioxide producing reactions. In the following

figures the reaction rate ratios r_1/r_3 , carbon dioxide production, and r_2/r_4 , carbon monoxide production rates are depicted for the two different temperatures.

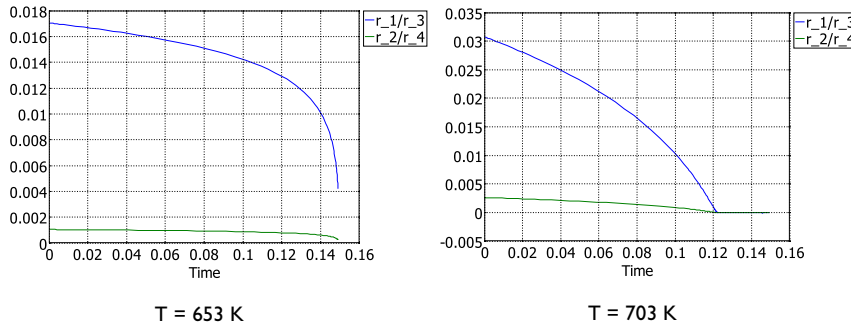


Figure 4-21: Relationship between the non-catalytic and catalytic carbon-oxidation reactions.

Figure 4-21 shows that the catalytic reactions by far dominate the oxidation of carbon. This is expected at these relatively moderate temperatures. The oxidation of carbon to carbon dioxide has a higher fraction of non-catalyzed oxidation than that of carbon to carbon monoxide. The dominance of the catalytic reactions decreases with temperature.

THE 2D MODEL

Figure 4-22 shows the initial velocity distribution in a channel unit cell. The flow regime is laminar.

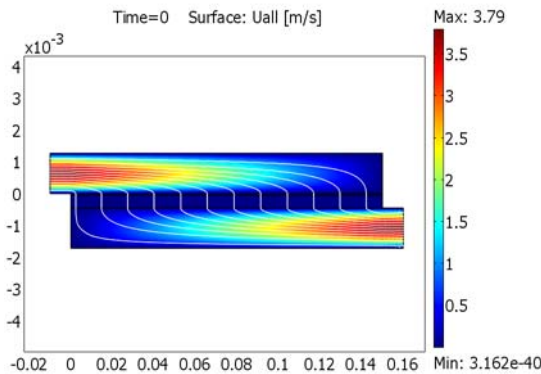


Figure 4-22: Velocity magnitude in a filter unit cell.

Figure 4-23 shows the pressure distribution across the channel pair. The the main pressure drop is observed across the thin but dense soot layer deposited on top of the porous membrane.

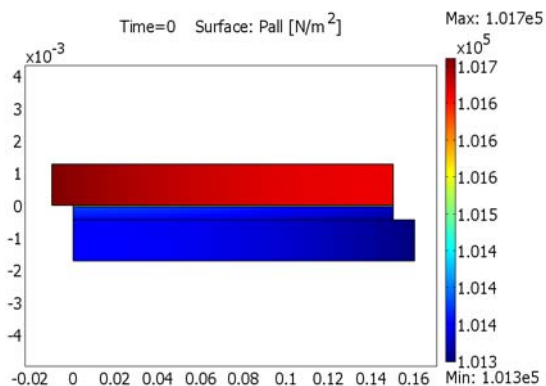


Figure 4-23: Pressure distribution in a filter unit cell.

The oxidation of carbon is overall an exothermic reaction, although the catalytic steps are endothermic. The regeneration of the catalyst is heavily exothermic and makes up for the endothermic properties of the catalytic oxidation reaction. The next figure shows the temperature distribution in the system after 300 s for an inlet temperature of 550 K. The exhaust gases leaves the filter at somewhat elevated temperatures due to the net exothermicity of the reactions.

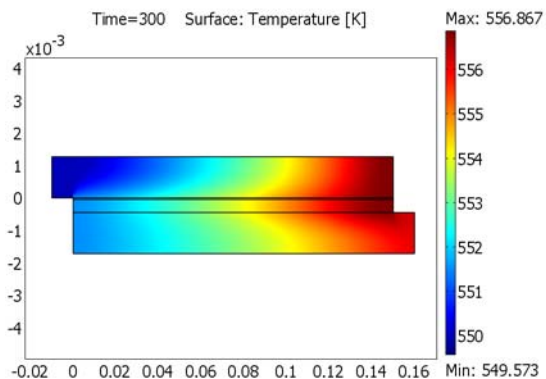


Figure 4-24: Temperature distribution in the filter for an inlet temperature of 550 K.

The following illustration (Figure 4-25) shows the soot layer along the length of the reactor at an inlet temperature of 550 K. The base-line corresponds to the initial soot layer thickness of 50 μm . The artifact at $x = 0$ appears because you do not allow the soot layer to grow or decrease at this position. Under the present conditions, carbon oxidation is not sufficient to keep the soot layer from growing.

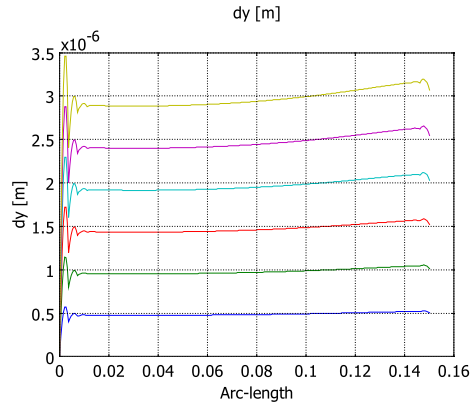


Figure 4-25: The soot layer's thickness at 0 to 300 s for 50 s intervals at an inlet temperature of 550 K. Time increases upwards in the plot.

Reference

I. G. Konstantas and A.M. Stamatelos, *Joint Meeting of the Greek and Italian Sections of the Combustion Institute*,
http://www.mie.uth.gr/labs/lte/pubs/Combust_Inst_Corfou_013.pdf.

Model Library path: Combustion/diesel_filter1

Model Library path: Combustion/diesel_filter2

The following path shows the location of the COMSOL Multiphysics model:

Model Library path:

Reaction_Engineering_Lab/Combustion/diesel_filter1

Modeling Using COMSOL Reaction Engineering Lab

You create a first model solely to export it to the Chemical Engineering Module and run it as a time-dependent 2D problem. However, prior to solving the space-dependent model in COMSOL Multiphysics you modify the reaction model so that it models a tube reactor and solve it in Reaction Engineering Lab.

MODEL NAVIGATOR

- 1 Start the Reaction Engineering Lab.
- 2 In the **Model Navigator**, click **New**.

MODEL SETTINGS

- 1 From the **Model** menu, select **Model Settings**.
- 2 Select the **Calculate thermodynamic properties** check box.
- 3 Select the **Calculate species transport properties** check box.
- 4 Select the **Include energy balance** check box.
- 5 Click **Close**.

REACTIONS SETTINGS—REACTION INTERFACE

- 1 From the **Model** menu, select **Reaction Settings**.
- 2 Create five entries in the **Reaction selection** list by clicking the **New** button repeatedly.
- 3 Enter the following reaction formulas by first selecting the appropriate row in the **Reaction selection** list and then typing the text in the **Formula** edit field.

REACTION ID #	REACTION FORMULA
1	$\text{c} + \text{o}_2 \Rightarrow \text{co}_2$
2	$\text{c} + 0.5\text{o}_2 \Rightarrow \text{co}$
3	$\text{c} + 4\text{ceo}_2 \Rightarrow 2\text{ce}_2\text{o}_3 + \text{co}_2$
4	$\text{c} + 2\text{ceo}_2 \Rightarrow \text{ce}_2\text{o}_3 + \text{co}$
5	$\text{ce}_2\text{o}_3 + 0.5\text{o}_2 \Rightarrow 2\text{ceo}_2$

- 4 On the **Kinetics** page, specify the following Arrhenius parameters by first selecting the appropriate row in the **Reaction selection** list, then selecting the **Use Arrhenius expressions** check box, and finally typing the corresponding numbers in the edit fields.

REACTION ID #	A (forward)	n (forward)	E (forward)
1	1e13	0	165e3
2	5.5e10	0	150e3
3	4.5e11	0	120e3
4	4e8	0	80e3
5	1e12	0	80e3

In this model you cannot evaluate the kinetics by applying the mass action law to the set of chemical reaction formulas you entered. Instead, alternative reaction rate expressions are used.

- 5 Select, one by one, the appropriate entry in the **Reaction selection** list, and replace the predefined reaction rates in the **r** edit field with the following reaction rate expressions:

REACTION ID #	r
1	$kf_1 * cO_c * c_o2$
2	$kf_2 * cO_c * c_o2$
3	$kf_3 * cO_c * c_ceo2$
4	$kf_4 * cO_c * c_ceo2$
5	$kf_5 * c_o2 * c_ce2o3$

- 6 Click the **Thermo** tab.

- 7 Type the following enthalpies of reaction in the **H** edit field after selecting the appropriate entry in the **Reaction selection** list:

REACTION ID #	H
1	-3.96e5
2	-1.1e5
3	6.72e4
4	1.21e5
5	-2.24e5

REACTION SETTINGS—SPECIES INTERFACE

- 1 Click the **Species** tab.
- 2 In the **Species selection** list, verify that six species were automatically generated from your reaction formulas: c, o2, co2, co, ceo2, and ce2o3.
- 3 On the **General** page, enter the following values for the initial concentrations in the **c₀** edit field after selecting the appropriate entry in the **Species selection** list.

SPECIES NAME	c ₀
o2	3.05
co2	1.525
co	1.525
ceo2	1
ce2o3	0

- 4 To remove the material balance of carbon, select the **Lock concentration/activity** check box after selecting **c** in the **Species selection** list. Specify **c₀** to 1.

Doing so not only removes the material balance, but also removes the species from expressions calculating properties of the reacting mixture.

Nitrogen is also present in the gas but does not take part in the reactions, so the next step is to add it as a species.
- 5 Create a new species entry by clicking **New** and then typing n2 in the **Formula** edit field.

In this model you also assume that nitrogen is the dominant species in the gas mixture and thus serves as a solvent in which the other species are diluted.
- 6 To define n2 as solvent, select it in the **Species selection** list and select **Solvent** from the **Type** list at the upper-right corner of the **Reaction Settings** dialog box.
- 7 Type 27.41 in the **c₀** edit field.

When a species has been selected as solvent, the physical properties of the gas phase mixture will be take to be those of the solvent species.
- 8 Enter the following values for the molecular weight in the **M** edit field after selecting the appropriate entry in the **Species selection** list. Note that you do not need to specify the molecular weights of the cerium species because they are solid and

therefore not transported. Due to their small concentration they also do not affect the fluid density.

SPECIES NAME	M
o2	32e-3
co2	44e-3
co	28e-3
ceo2	172e-3
ce2o3	328e-3
n2	28e-3

9 Click the **Thermo** tab.

10 From the **Species selection** list, select n2. Then type the following components in the **a_{low,k}** edit field for **Polynomial coefficients**:

COMPONENT #	n2
1	3.298677
2	0.14082404e-2
3	-0.03963222e-4
4	0.05641515e-7
5	-0.02444854e-10
6	-0.10208999e4
7	3.950372

11 Locate the **T_{int}** edit fields for the **Temperature interval limits**. In the **lower** edit field type 300; in the **midpoint** edit field type 3000; and in the **upper** edit field type 3000. With this setup you use a single temperature interval to describe nitrogen's thermodynamic properties.

12 Click the **Transport** tab.

- 13** Type the following interaction potential parameters in the ϵ/k_b and σ edit fields after selecting, one by one, the appropriate entries in the **Species selection** list:

SPECIES NAME	σ	ϵ/k_b
o2	3.467	106.7
co2	3.941	195.2
co	3.69	91.7
ceo2	1	50
ce2o3	1	50
n2	3.798	71.4

Note that you do not need any transport properties for the cerium species, since they will not be mobile. However, you must use some arbitrary numbers in this list for the export mechanism to work properly, since the Reaction Engineering Lab will try to calculate the diffusion coefficients anyway.

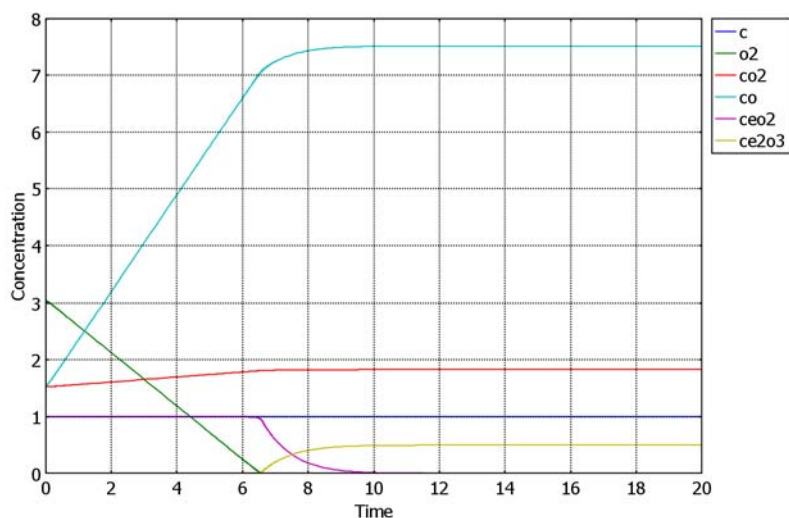
- 14** Click **Close**.

COMPUTING THE SOLUTION

The reaction model now describes a perfectly mixed tank reactor, with both mass and energy balances. This is what you will export to COMSOL Multiphysics in order to model the system as space dependent. However, prior to exporting, it is generally a good idea to solve the model in order to verify that there are no problems.

- 1 Click the **Model Settings** button on the Main toolbar, and then select the **Energy Balance** page.
- 2 In the Q_{ext} edit field for the **External heat source**, type $-15/1.25e-3*(T-473.15)$.
- 3 Select the **Init** page and type 473.15 in the $T(t_0)$ edit field for the **Initial temperature**.
- 4 Click **Close**.
- 5 Click the **Solve Problem** button (=) on the Main toolbar.
The default plot, shows the concentration of all species. To produce the plot below remove the concentration for n2.
- 6 Click the **Plot Parameters** button and use the < button to remove **n2** from the **Quantities to plot** list on the right.

7 Click **OK**, and you should get the following figure.



8 Using the menu item **File>Save As**, you can now save the model for later use (name the model `diesel_filter1.rxn`).

1D Tubular Reactor

The situation in the filter system can be described as a 1D tubular reactor. You then use Reaction Engineering Lab to solve for the profiles with respect to position in the reactor. In order to do so, the differential equations produced by Reaction Engineering Lab for the filter are altered according to Equation 4-52. In addition, the model is solved for as being isothermal. Thus, the energy balance is omitted and a constant temperature is prescribed.

MODEL SETTINGS

- 1 From the **Model** menu, select **Model Settings**.
- 2 Clear the **Include energy balance** check box.
- 3 Type 653 in the **Temperature** edit field.
- 4 Click **Close**.

CONSTANTS AND EXPRESSIONS

- 1 From the **Model** menu select **Constants**.
- 2 Specify the following entries by typing in **Name**, **Expression**, and **Description**, at completion click **OK**.

NAME	EXPRESSION	DESCRIPTION
L	0.15	Reactor Length (m)
u0	2.5	Inlet velocity (m/s)
ku	-u0/L	Proportionality constant
H	1.27e-3	Channel height (m)
vf	u0*H/L	Filter gas velocity (m/s)
Sa	5e-5/H	Surface area factor

- 3 From the **Model** menu select **Expressions**.
- 4 Specify the following entries by typing in **Name**, **Expression**, and **Description**, at completion click **OK**.

NAME	EXPRESSION	DESCRIPTION
u	u0+ku*t	Local channel velocity (m/s)

REACTIONS SETTINGS—REACTION INTERFACE

Modify the reaction rates in order to take the difference in domain thickness between the catalyzing layer (0.05 mm thick) and the channel (1.27 mm). This is achieved by multiplying all reaction rates with the constant Sa.

- 1 From the **Model** menu, select **Reaction Settings**.
- 2 Edit the Arrhenius parameter for the **Frequency factor** by multiplying the present value with the constant Sa. This is done for each one of the five reactions. Thus type in *Sa after the numeral value for each reaction.

REACTION SETTINGS—SPECIES INTERFACE

Now modify the mass balances according to Equation 4-52.

- 1 Click the **Species** tab.

- For each species listed in the table below, replace the **Rate expression** by typing in the indicated expression in the **R** edit field.

SPECIES NAME	Rate expression
o2	$((-r_1 - 0.5*r_2 - 0.5*r_5) - ku*c_{o2} - vf/H*c_{o2})/u$
co2	$((r_1 + r_3) - ku*c_{co2} - vf/H*c_{co2})/u$
co	$((r_2 + r_4) - ku*c_{co} - vf/H*c_{co})/u$
ceo2	$((-4*r_3 - 2*r_4 + 2*r_5) - ku*c_{ceo2} - vf/H*c_{ceo2})/u$
ce2o3	$((2*r_3 + r_4 - r_5) - ku*c_{ce2o3} - vf/H*c_{ce2o3})/u$
n2	$-(ku*c0_{n2} + vf/H*c0_{n2})/u$

- Select species **n2** and clear the **Lock concentration/activity** check box.
- Click **Close**.

COMPUTING THE SOLUTION

Now the model describes the position in the reactor with the independent variable t . This means that you have to specify the integration limit to be equal to the reactor length.

- From the **Simulation** menu, select **Solver Parameters**.
- Type 0.149 in the **Times** edit field. You use 0.149 to avoid describing the stagnant zone close to the dead-end of the tubular reactor.
- Click **OK**, and then click the **Solve Problem** button on the Main toolbar.

POSTPROCESSING

The produced plot should resemble the left panel of Figure 4-20. To produce the left panel of Figure 4-21 follow these steps:

- Click the **Plot Parameters** button. Click **<<** to clear the **Quantities to plot** list.
- Type r_1/r_3 in the **Expression** edit field and click **>** to add it to the **Quantities to plot** list.
- Type r_2/r_4 in the **Expression** edit field and click **>** to add it to the **Quantities to plot** list.
- Click **OK**.

In order to calculate the results for the higher temperature use **Model>Model Settings** to change the **Temperature** to 703, then click the **Solve Problem** button. Generate the right panel of Figure 4-20 and Figure 4-21 by repeating steps 1 to 3 above.

- 5 Use the menu item **File>Save As** to save the model for later use (name the model `diesel_filter2.rxn`).

Modeling Using COMSOL Multiphysics

You first generate a moving-mesh model of the filtration process before actually exporting the kinetic model from the Reaction Engineering Lab into the Chemical Engineering Module.

MODEL NAVIGATOR

- 1 Start COMSOL Multiphysics.
- 2 From the list of application modes, select
COMSOL Multiphysics>Deformed Mesh>Moving Mesh (ALE)>Transient analysis.
- 3 Click the **Multiphysics** button, then click **Add**.
- 4 From the list of application modes, select
Chemical Engineering Module>Flow with Variable Density>Weakly Compressible Navier-Stokes>Transient analysis
- 5 Click **Add**.
- 6 From the list of application modes, select
Chemical Engineering Module>Momentum Transport>Porous Media Flow>Darcy's Law>Transient analysis.
- 7 Click **Add**.
- 8 Click **OK**.

OPTIONS AND SETTINGS

- 1 Choose **Options>Constants**.
- 2 Enter constants according to the table below in the **Constants** dialog box.

NAME	EXPRESSION
visc	3e-5
kappa	1e-11
kappa1	1e-13
Tin	550
cpn2	1532
kn2	0.06
densn2	0.525

NAME	EXPRESSION
kmix	30
Pat	1.013e5
poro	0.5
paco	5e-4
pade	1920
Mc	12e-3
des	5e-5

3 Click **OK**.

4 From the **Options>Expressions** menu, select **Scalar Expressions** and enter expressions according to the table below.

NAME	EXPRESSION
dx	dx_ale
dy	dy_ale

5 Click **OK**.

GEOMETRY MODELING

1 Hold the Shift key and click the **Rectangle/Square** button on the Draw toolbar. Enter the values for rectangle R1 from the following table. Repeat the procedure for rectangles R2 through R6.

PROPERTY	R1	R2	R3	R4	R5	R6
Width	1e-2	0.15	0.15	0.15	0.15	1e-2
Height	1.27e-3	1.27e-3	5e-5	4e-4	1.27e-3	1.27e-3
Base	Corner	Corner	Corner	Corner	Corner	Corner
x	-1e-2	0	0	0	0	0.15
y	0	0	-5e-5	-4.5e-4	-1.72e-3	-1.72e-3

2 Click **OK**.

3 Double-click **EQUAL** on the status bar at the bottom of the user interface and then click the **Zoom Extents** button on the Main toolbar.

4 With the mouse, select rectangles R1 and R2 (Ctrl-click), then click the **Create Composite Object** button on the Draw toolbar.

5 Clear the **Keep interior boundaries** check box, then click **OK**.

- 6 With the mouse, select rectangles R5 and R6, then click the **Create Composite Object** button on the Draw toolbar.
- 7 Make sure that the **Keep interior boundaries** check box is cleared.
- 8 Click **OK**.
- 9 From the **Options>Expressions** menu, select **Subdomain Expressions** and define expressions according to the table below.

NAME	EXPRESSION IN SUBDOMAINS 1 & 2	EXPRESSION IN SUBDOMAIN 3 & 4
uall	u	u_chd1
vall	v	v_chd1
Uall	$\sqrt{uall^2+vall^2}$	$\sqrt{uall^2+vall^2}$
Pall	p	p2

- 10 Click **OK**.

PHYSICS SETTINGS

Subdomain Settings—Weakly Compressible Navier-Stokes

- 1 Choose **Multiphysics>Weakly Compressible Navier-Stokes (chns)**.
- 2 Choose **Physics>Subdomain Settings**.
- 3 From the **Subdomain selection** list, select **1** and **2**.
- 4 In the **Dynamic viscosity** edit field, type **visc**.
- 5 Go to the **Density** page and type **densn2** in the **p** edit field.
- 6 Click the **Init** tab, and type **Pat** in the **Pressure** edit field.
- 7 From the **Subdomain selection** list, first click to select **3** and then Ctrl-click **4**.
- 8 Clear the **Active in this subdomain** check box.
- 9 Click **OK**.
- 10 Choose **Physics>Properties**.
- 11 From the **Weak constraints** list, select **On**.
- 12 From the **Constraint type** list, select **Non-ideal**.
- 13 Click **OK**.

Subdomain Settings—Darcy's Law

- 1 Choose **Multiphysics>Darcy's Law (chdl)**.
- 2 Choose **Physics>Subdomain Settings**.

- 3 In the **Subdomain selection** list, Ctrl-click to select **1** and **2**.
- 4 Clear the **Active in this subdomain** check box.
- 5 From the **Subdomain selection** list, select **3**.
- 6 In the **Porosity** edit field, type poro.
- 7 In the **Density** edit field, type densn2.
- 8 In the **Permeability** edit field, type kappa.
- 9 In the **Dynamic viscosity** edit field, type visc.
- 10 Click the **Init** tab and in the **Pressure** edit field, type Pat.
- 11 Click the **Physics** tab.
- 12 In the **Subdomain selection** list, select **4**.
- 13 In the **Porosity** edit field, type poro.
- 14 In the **Permeability** edit field, type kappa1.
- 15 In the **Density** edit field type densn2.
- 16 In the **Dynamic viscosity** edit field, type visc.
- 17 Click the **Init** tab, and in the **Pressure** edit field, type Pat.
- 18 Click **OK**.
- 19 Choose **Physics>Properties**.
- 20 From the **Weak constraints** list, select **On**.
- 21 From the **Constraint type** list, select **Non-ideal**.
- 22 Click **OK**.

Subdomain Settings—Moving Mesh (ALE)

- 1 From the **Multiphysics** menu, select **Moving Mesh (ALE) (ale)**.
- 2 Choose **Physics>Subdomain Settings**.
- 3 From the **Subdomain selection**, list select **2** and **3**.
- 4 Click to select the **no displacement** button.
- 5 Click **OK**.

Boundary Conditions—Weakly Compressible Navier-Stokes

- 1 Choose **Multiphysics>Weakly Compressible Navier-Stokes (chns)**.
- 2 Choose **Physics>Boundary Settings**.

- 3 Make selections from the **Boundary selection** list and enter the corresponding settings:

SETTINGS	BOUNDARY 1	BOUNDARY 7	BOUNDARY 10	BOUNDARY 17	ALL OTHERS
Boundary type	Inlet	Inlet	Outlet	Outlet	Wall
Boundary condition	Velocity	Velocity	Velocity	Pressure, no viscous stress	No slip
u_0	$15 \cdot s \cdot (1 - s)$	$-\kappa / \text{visc} \cdot p_{2x}$	$-\kappa_{11} / \text{visc} \cdot p_{2x}$		
v_0		$-\kappa / \text{visc} \cdot p_{2y}$	$-\kappa_{11} / \text{visc} \cdot p_{2y}$		

- 4 Click **OK**.

Boundary Conditions—Darcy's Law

- 1 Choose **Multiphysics>Darcy's Law (chdl)**.
- 2 Choose **Physics>Boundary Settings**.
- 3 Make selections from the **Boundary selection** list and enter the following settings:

SETTINGS	BOUNDARIES 7, 10
Boundary condition	Pressure condition
p_0	p

For all other active boundaries, keep the default **Insulation/Symmetry** condition.

- 4 Click **OK**.

Boundary Conditions—Moving Mesh (ALE)

- 1 Choose **Multiphysics>Moving Mesh (ALE) (ale)**.
- 2 Choose **Physics>Boundary Settings**.
- 3 Select all boundaries, then select the **dx** and **dy** check boxes to prevent any displacements.
- 4 Select Boundaries 8, 15, and 16, then clear the **dy** check box.
- 5 Select the **Interior boundaries** check box.
- 6 Select Boundary 10.
- 7 Select the **Mesh velocity** option button.

- 8 Select the **vy** check box and type `-paco/pade*v` in the corresponding edit field.
Doing so displaces the boundary in proportion to the flow velocity across it and the particle density in the incoming flow.
- 9 Click **OK**.

MESH GENERATION

- 1 From the **Mesh** menu, select **Mapped Mesh Parameters**.
- 2 Click the **Boundary** tab, select all boundaries, and check the **Constrained edge element distribution** check box. Then define the **Number of edge elements** as in this table:

SETTING	BOUNDARIES 5, 7, 9–11	BOUNDARIES 8, 15	ALL OTHERS
Number of edge elements	40	1	5

- 3 Click **Remesh**.
- 4 Click **OK**.

EXPORTING FROM THE REACTION ENGINEERING LAB

- 1 In COMSOL Multiphysics choose **File>Reaction Engineering Lab**. This selection opens the Reaction Engineering Lab.
- 2 Choose **File>Open**. In the **Open Model** dialog box, browse to the model `diesel_filter1.rxn` that you created earlier in this exercise.
- 3 Click **Open**.
- 4 Click the **Export to COMSOL Multiphysics** button.
- 5 A new dialog box appears. In the **Export mass balance** area, go to the **Application mode** list and select **Convection and Diffusion: New**.
- 6 In the corresponding **Group name** edit field, type `mat_bal`.
- 7 In the **Export energy balance** area, go to the **Application mode** list and select **Convection and Conduction: New**.
- 8 In the corresponding **Group name** edit field, type `en_bal`.
- 9 Clear the **Export momentum balance** check box.
- 10 Click **Export**.
- 11 Exit the Reaction Engineering Lab.

You can now continue the modeling procedure in COMSOL Multiphysics.

PHYSICS SETTINGS

Subdomain Settings—Convection and Diffusion

- 1 Choose **Multiphysics>Convection and Diffusion (chcd)**.
- 2 Choose **Physics>Subdomain Settings**.
- 3 Go to the **Subdomain selection** list and select all the entries.
- 4 From the **Group** list (just below the **Subdomain selection** list), select **mat_bal**.
- 5 For **c_o2**, **c_co2**, and **c_co**, find the **x-velocity** edit field and type **ua11**, then find the **y-velocity** edit field and type **va11**.
- 6 Click the **c_ceo2** tab. In the **Diffusion coefficient** edit field, type **1e-10**. (Note that you delete the unwieldy expression created by the Reaction Engineering Lab.)
- 7 Click the **c_ce2o3** tab. In the **Diffusion coefficient** edit field, type **1e-10**.
- 8 Click **Apply**.
- 9 From the **Subdomain selection** list, select 1, 2, and 3.
- 10 Replace the expression in the **Reaction rate** edit field with 0 for all species. Do so in order to neglect the reaction in the bulk of the fluid.
- 11 Click **OK**.

Subdomain Settings—Convection and Conduction

- 1 Choose **Multiphysics>Convection and Conduction (chcc)**.
- 2 Choose **Physics>Subdomain Settings**.
- 3 Go to the **Subdomain list** and select all the entries.
- 4 From the **Group** list, select **en_bal**.
- 5 In the **x-velocity** edit field, type **ua11**, and in the **y-velocity** edit field, type **va11**.
- 6 Click the **Init** tab, find the **Temperature** field, and type **Tin**.
- 7 Click **Apply**.
- 8 Click the **Physics** tab.
- 9 From the **Subdomain list**, select 1, 2, and 3.
- 10 Replace the expression in the **Heat source** edit field with 0.
- 11 Click **Apply**.
- 12 From the **Subdomain list**, select 3 and 4.
- 13 Replace the expression in the **Thermal conductivity** edit field with **kmix**.
- 14 Click **OK**.

Boundary Settings

- 1 Choose **Multiphysics>Convection and Diffusion (chcd)**.
- 2 Choose **Physics>Boundary Settings**.
- 3 Apply the boundary conditions from the following table for all species, then click **OK**.

BOUNDARY	c_o2	c_co2	c_co	c_ceo2	c_ce2o3
I	Conc.	Conc.	Conc.	Conc.	Conc.
	3.05	1.525	1.525	1	0
17	Convect. flux	Convect. flux	Convect. flux	Convect. flux	Convect. flux
All others	Insulation	Insulation	Insulation	Insulation	Insulation

- 4 Choose **Multiphysics>Convection and Conduction (chcc)**.
- 5 Choose **Physics>Boundary Settings**.
- 6 Set the boundary conditions as in the table below, then click **OK**.

SETTINGS	BOUNDARY I	BOUNDARY 17
Boundary condition	Temperature	Convective flux
T_0	T_{in}	

For all other active boundaries, keep the default **Thermal insulation** condition.

- 7 Choose **Multiphysics>Moving Mesh (ALE) (ale)**.
- 8 Choose **Physics>Boundary Settings**.
- 9 From the **Boundary** list, select **10**.
- 10 Select the **Mesh velocity** option button.
- 11 Select the **vy** check box and replace the expression in the associated edit field with

$$-paco/pade*v+Mc/pade*(dy+des)*$$

$$(r_1_rxn_chcd+r_2_rxn_chcd+r_3_rxn_chcd+r_4_rxn_chcd)$$
. This expression includes the reactions that consume the soot particles.
- 12 Click **OK**.

COMPUTING THE SOLUTION

In a model described by a strongly coupled system of equations, it is often a good practice to solve the problem sequentially to avoid convergence issues. Here you start by solving for the stationary flow. After that, you couple the mass and energy balances

to the flow. Finally, you solve the full time-dependent system, with the dynamic nature of the soot layer handled by the Moving Mesh (ALE) application mode.

- 1 Click the **Solver Parameters** button on the Main toolbar.
- 2 From the **Solver** list, select **Stationary**.
- 3 Click **OK**.
- 4 Click the **Solver Manager** button on the Main toolbar.
- 5 Click the **Solve For** tab.
- 6 From the list of application modes, select **Weakly Compressible Navier-Stokes** and **Darcy's Law**.
- 7 Click the **Solve** button on the Main toolbar.
- 8 In the list of application modes, select all application modes except **Moving Mesh (ALE)**.
- 9 Click **OK**.
- 10 Click the **Restart** button on the Main toolbar.
- 11 Click the **Solver Parameters** button on the Main toolbar.
- 12 From the **Solver** list, select **Time dependent**.
- 13 In the **Times** edit field, type 0:10:300.
- 14 Click **OK**.
- 15 Click the **Solver Manager** button on the Main toolbar.
- 16 Click the **Solve For** tab. Press Ctrl+A to select all variables.
- 17 Click **OK**.
- 18 Click the **Restart** button on the Main toolbar.

POSTPROCESSING

To reproduce the plot in Figure 4-22 do the following steps.

- 1 Open the **Plot Parameters** dialog box.
- 2 On the **General** page set **Solution at time** to 0.
- 3 Go to the **Surface** page and type Ua11 in the **Expression** edit field.
- 4 Go to the **Streamline** page, select **Streamline plot** and type ua11 and va11 as X and Y component respectively.
- 5 Set **Streamline plot type** to **Magnitude controlled**.
- 6 On the **Line Color** page set the **Uniform color** to white.

7 Click **OK**.

Create the plot in Figure 4-23 with the following steps.

- 1 Open the **Plot Parameters** dialog box and clear the **Streamline plot** check box
- 2 Go to the **Surface** page and type Pa11 in the **Expression** edit field.
- 3 Click **OK**.

The following steps reproduces Figure 4-24.

- 1 Open the **Plot Parameters** dialog box.
- 2 On the **Surface** page type T in the **Expression** edit field.
- 3 Go to the **General** page and set **Solution at time** to 300.
- 4 Click **OK**.

To create the plot in Figure 4-25 do the following steps.

- 1 Open the **Domain Plot Parameters** dialog box from the **Postprocessing** menu.
- 2 Select 0, 50, 100, 150, 200, 250 and 300 from the **Solutions to use** list.
- 3 On the **Line/Extrusion** page select Boundary 9 and select **y-displacement** in the **Predefined quantities** list.
- 4 Click **OK**.

Selective Catalytic Reduction of NO_x

Introduction

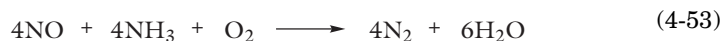
The removal of pollutants from high-temperature gases is often required in combustion processes. In this example, the selective reduction of NO_x by ammonia occurs as flue gas passes through a honeycomb reactor. The chemical reactions take place on the surface of a V₂O₅/TiO₂ catalyst that is supported on a ceramic structure.

This example shows how to use the COMSOL Reaction Engineering Lab in concert with the Chemical Engineering Module to readily solve advanced engineering problems. You can start by setting up the reaction kinetics in the Reaction Engineering Lab and then model the chemistry assuming that each of the channels in the monolith behaves as a plug-flow reactor. This gives you a notion about the magnitude of important design parameters such as the residence time and selectivity as a function of temperature. In a second part of the example, you set up a reactor model taking the actual geometry of a monolith channel into account by exporting the reaction model from Reaction Engineering Lab to the Chemical Engineering Module. In the space-dependent model you can solve the mass-balance equations coupled to the momentum balances for free flow and porous media flow.

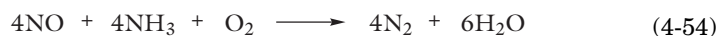
Note: Solving the second part of this model requires the Chemical Engineering Module.

Model Definition

NO reduction by ammonia can be summarized by the following reaction:



However, ammonia can at the same time undergo oxidation:



When optimizing the conversion of NO, you consequently seek to minimize the oxidation reaction while maintaining a reasonable reaction rate for the reduction.

The heterogeneous catalytic conversion of NO to N₂ is described by an Eley-Rideal mechanism. A key reaction step involves the reaction of gas-phase NO with surface-adsorbed NH₃. The following rate equation (mol/(m³·s)) has been suggested in Ref. 1 for Equation 4-53:

$$r_1 = k_1 c_{\text{NO}} \frac{a c_{\text{NH}_3}}{1 + a c_{\text{NH}_3}} \quad (4-55)$$

where

$$k_1 = A_1 \exp\left(-\frac{E_1}{R_g T}\right) \quad (4-56)$$

and

$$a = A_0 \exp\left(-\frac{E_0}{R_g T}\right) \quad (4-57)$$

For Equation 4-54, the reaction rate (mol/(m³·s)) is given by

$$r_2 = k_2 c_{\text{NH}_3} \quad (4-58)$$

where

$$k_2 = A_2 \exp\left(-\frac{E_2}{R_g T}\right) \quad (4-59)$$

This example investigates the conversion of NO_x through two reactor models. You first set up and solve a plug-flow reactor in the COMSOL Reaction Engineering Lab, and then you solve a space-dependent reactor model using COMSOL Multiphysics.

Assuming steady, the design equation for a plug-flow reactor is given by:

$$\frac{dF_i}{dV} = R_i \quad (4-60)$$

where F_i is the species molar flow rate (mol/s), V represents the reactor volume (m³), and is R_i the species net reaction rate (mol/(m³·s)). The molar flow rate is related to the species concentrations, c_i (mol/m³), through the volumetric flow rate, v (m³/s):

$$F_i = v c_i \quad (4-61)$$

where the volumetric flow rate is given by the average flow velocity, u (m/s), multiplied by the reactor cross-section A (m²):

$$v = uA \quad (4-62)$$

The mass balances given by Equation 4-60 are set up and solved in the Reaction Engineering Lab.

The plug-flow model considerably simplifies the reaction conditions compared to actual reactors used in industry. In the extended example, the conversion of NO_x occurs in a honeycomb reactor, which consists of packets of thin parallel channels through which the flue gas flows. The ceramic channel walls are coated with a porous catalytic layer, in this case V₂O₅/TiO₂.

The transport and reaction of chemical species can be divided into several steps: First the reactants are transported in the direction of the flow, mainly by convection in the open channels. The reactants diffuse towards the walls and into the porous catalyst where they react on the catalyst surface. Formed products subsequently diffuse out of the porous structure and are transported out of the reactor through the open channels.

The model setup in COMSOL Multiphysics corresponds to a single channel of the honeycomb structure. The model assumes the channel is cylindrical, making it possible to reduce the modeling domain to a 2D geometry with rotational symmetry. The model geometry appears in Figure 4-26.

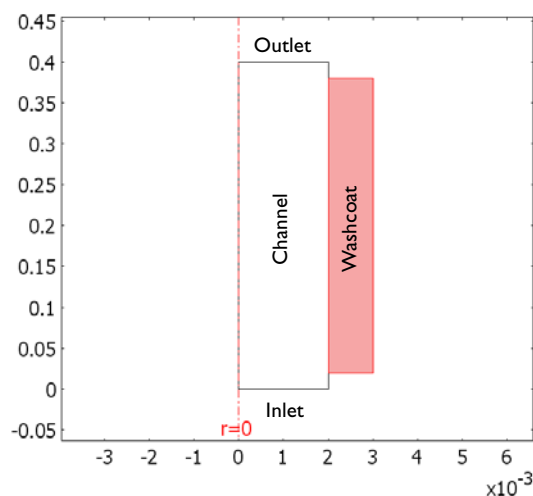


Figure 4-26: Geometry of a reactor-channel model taking axial symmetry into account. Dimensions are in meters (m).

MOMENTUM TRANSPORT

The flow in the free channel is described by the Navier-Stokes equations:

$$\begin{aligned}\nabla \cdot [-\eta(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) + p\mathbf{I}] &= -\rho(\mathbf{u} \cdot \nabla)\mathbf{u} \\ \nabla \cdot \mathbf{u} &= 0\end{aligned}\quad (4-63)$$

where ρ denotes density (kg/m^3), \mathbf{u} represents the velocity (m/s), η denotes viscosity ($\text{kg}/(\text{m} \cdot \text{s})$), and p equals pressure (Pa). In the porous domain, the Brinkman equations describe the flow:

$$\begin{aligned}\nabla \cdot \left[-\frac{\eta}{\varepsilon_p}(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) + p\mathbf{I} \right] &= -\frac{\eta}{k}\mathbf{u} \\ \nabla \cdot \mathbf{u} &= 0\end{aligned}\quad (4-64)$$

Here ε_p denotes the porosity (dimensionless) and k refers to the permeability (m^2) of the porous medium. As you can see in Equation 4-63 and Equation 4-64, the momentum-balance equations are closely related. The term on the right-hand side of the Navier-Stokes formulation corresponds to momentum transported by convection in free flow. In the Brinkman formulation, this term is replaced by a contribution associated with the drag force experienced by the fluid as it flows through a porous medium. COMSOL Multiphysics effortlessly combines free flow and porous-media flow.

The boundary conditions are

$$\begin{aligned}\mathbf{u} \cdot \mathbf{n} &= v_0 && \text{inlet} \\ \mathbf{u} &= \mathbf{0} && \text{walls} \\ p &= p_{\text{ref}} && \text{outlet}\end{aligned}\quad (4-65)$$

At the outlet viscous stresses are ignored and the pressure is set to 1 atmosphere.

MASS TRANSPORT

The mass-balance equations for the model are the diffusion-convection equations at steady state:

$$-\nabla \cdot (-D_i \nabla c_i + c_i \mathbf{u}) = R_i \quad (4-66)$$

Here D_i denotes the diffusion coefficient (m^2/s), c_i is the species concentration, and \mathbf{u} equals the velocity vector (m/s). The term R_i corresponds to the species' net reaction rate, which is a function of the reaction rates, Equation 4-55 and Equation 4-58, and the reaction stoichiometry.

In the free channel, the inlet conditions are equal to the inlet concentrations:

$$c = c_{\text{in}} \quad (4-67)$$

At the outlet, use the convective flux condition

$$\mathbf{n} \cdot (-D\nabla c) = 0 \quad (4-68)$$

All other boundaries use the insulating or symmetry condition

$$\mathbf{n} \cdot (-D\nabla c + c\mathbf{u}) = 0 \quad (4-69)$$

TRANSPORT PROPERTIES

Setting up momentum and mass balances requires that certain physical properties characteristic of the reacting fluid are determined. For instance, the Navier-Stokes equation (Equation 4-63) and the Brinkman equation (Equation 4-64) both require the fluid viscosity. Furthermore, the mass balances need species specific diffusion coefficients as input.

For reacting gas mixtures, the Reaction Engineering Lab makes use of kinetic gas theory to set up expressions for transport properties such as binary diffusivities, viscosity, and thermal conductivity as functions of temperature, pressure, and composition. In this example, the diffusivities (m^2/s) are calculated using the formula:

$$D = 2.695 \cdot 10^{-3} \cdot \frac{\sqrt{T^3((M_A + M_B)/(2 \cdot 10^3 M_A M_B))}}{p \sigma_A \sigma_B \Omega_D} \quad (4-70)$$

where Ω_D is a collision integral

$$\Omega_D = f\left(T, \sigma, \frac{\varepsilon}{k}, \mu\right). \quad (4-71)$$

Furthermore gas viscosity (Ns/m^2) is given by the expression:

$$\eta = 2.699 \cdot 10^{-6} \cdot \frac{\sqrt{T(1 \cdot 10^3 M)}}{\sigma^2 \Omega_v} \quad (4-72)$$

where Ω_v is a collision integral

$$\Omega_v = f\left(T, \sigma, \frac{\varepsilon}{k}, \mu\right). \quad (4-73)$$

To evaluate Equation 4-70 and Equation 4-72, you need to specify the characteristic length and energy minimum of the Lennard-Jones interaction potential, that is σ (10^{-10} m) and the ϵ/k (K), respectively. The species dipole moment, μ (Debye), can also be provided. Each species in the reacting gas has a characteristic set of these constants, and you find their values in the literature, in databases, or from experiments. The parameters σ , ϵ/k , and μ can either be entered manually in the Reaction Engineering Lab GUI, or you can import text files containing the data. In this model you import transport data using the **Import CHEMKIN File** feature.

The structure of a CHEMKIN transport data file is illustrated below:

NO	0	97.500	3.620	0.000	0.000	0.000
NH3	0	558.300	2.900	1.470	0.000	0.000
O2	0	106.700	3.470	0.000	0.000	0.000
N2	0	71.400	3.800	0.000	0.000	0.000
H2O	0	809.100	2.640	1.880	0.000	0.000

The first column indicates the species name; the second column contains an index describing the geometrical configuration of the molecule; the third column provides the value for ϵ/k ; the fourth column lists the value for σ ; the fifth column gives the value of μ ; the sixth column indicates polarizability; and the seventh column lists rotational relaxation collision number.

The entries given in columns 1, 3, 4, and 5 are read into the Reaction Engineering Lab when selecting the menu item **File>Import>CHEMKIN Transport Input File**.

Resources for kinetic, thermodynamic, and transport data on the CHEMKIN format are available on the web (see, for instance, www.comsol.com/reaction).

Results

First review the results of the plug-flow model, which you set up and solve in the Reaction Engineering Lab.

Figure 4-27 shows the concentrations of NO and NH₃ as functions of the reactor volume. Reactions take place at 523 K and that the gas enters the reactor with a velocity of 0.3 m/s. The reactor is assumed to be a channel with a length of 0.36 m

and a radius of 2 mm. Under these conditions, the simulations show that most of the NO has been converted as the gas leaves the reactor (NO converted > 99%).

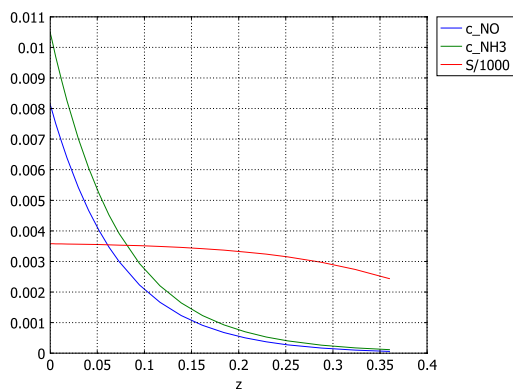


Figure 4-27: Concentrations of NO and NH_3 as functions of axial distance from the reactor inlet. S is the selectivity parameter.

The plot also shows the selectivity parameter, S , giving the ratio of reaction rates according to

$$S = \frac{r_1}{r_2} \quad (4-74)$$

S varies between 3.6 and 2.7 along the reactor length, indicating that the reduction of NO is the dominating reaction pathway.

Figure 4-28 shows the initial reaction rate of NO reduction (r_1) and NH_3 oxidation (r_2) in the temperature interval 450–750 K. Up to approximately 655 K, NH_3 is mainly consumed by the desired reduction reaction, Equation 4-53. At about 670 K the rate of NO reduction reaches a maximum. Above this temperature the desorption

of NH_3 from the catalyst surface becomes faster than the reaction of adsorbed NH_3 with gas-phase NO .

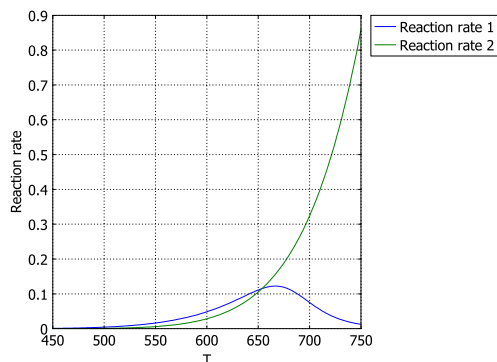


Figure 4-28: Initial rates of NO reduction (Reaction rate 1) and NH_3 oxidation (Reaction rate 2) as functions of temperature for the plug-flow reactor model.

The following results come from the space-dependent reactor model, which you set up and solve in COMSOL Multiphysics. In this case, the chemistry takes place in a channel of a honeycomb reactor.

Figure 4-29 shows the fluid velocity profile, given as a function of radial position at the channel midpoint.

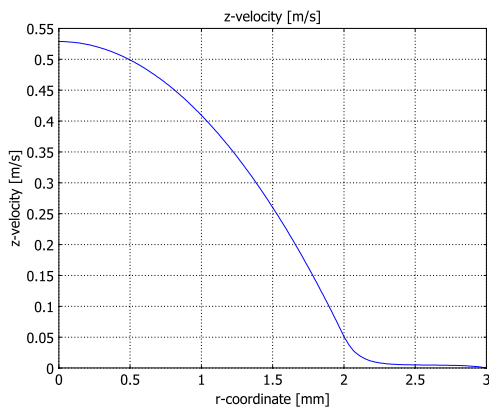


Figure 4-29: Flow velocity as a function of radial position.

Figure 4-30 displays the concentration of NO across the reactor channel. Integrating the boundary flux of NO across the inlet and outlet allows you to calculate the conversion of NO as being 89%.

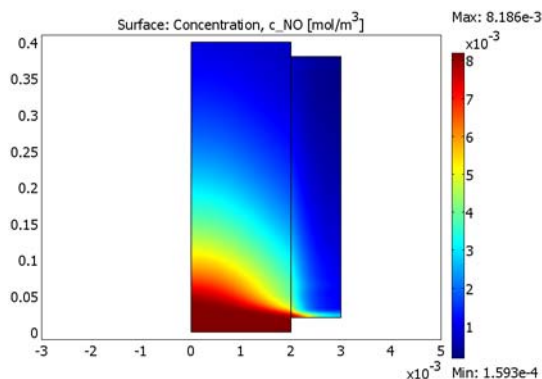


Figure 4-30: Concentration of NO across the space-dependent model domain.

It is easy to extend the model to study the effects of different design parameters such as reaction temperature, inlet velocity, and geometry. It can also easily take into account the effect of material properties such as the permeability of the porous region.

Figure 4-31 compares the results of the plug-flow model and the reactor model including the actual channel geometry. For the channel model, the NO concentration shown is the average concentration evaluated along the section of channel length affected by the catalytic washcoat (0.36 m). The average inlet velocity in the channel model is 0.3 m/s.

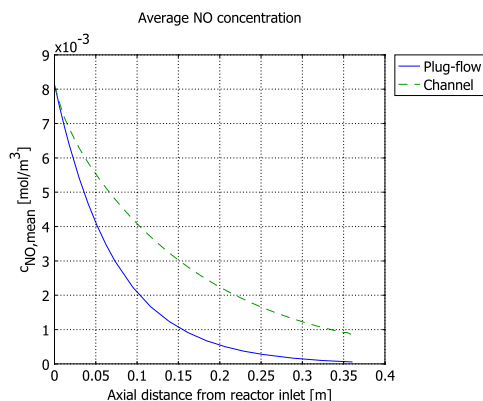


Figure 4-31: Concentration of NO (mol/m^3) along the reactor channel. The solid line represents data from the plug-flow model and the dashed line represents the mean concentration evaluated from the channel model.

The assumptions underlying the plug-flow model readily explain the differences in results. In the plug-flow model, reactions are assumed to occur homogeneously throughout the reactor volume. Because the species need not be transported to and from the bulk flow to the reactive washcoat, as is the case in the channel model, the conversion of reactants is, of course, faster.

In summary: This example illustrates the modeling of a heterogeneous catalytic process using the COMSOL Reaction Engineering Lab and the Chemical Engineering Module. The Reaction Engineering Lab helps you set up the chemical kinetics and expressions describing the transport properties of the reacting mixture. In COMSOL Multiphysics you study the reacting flow in a specific reactor geometry.

Reference

1. G. Shaub, D. Unruh, J. Wang, and T. Turek, *Chemical Engineering and Processing*, vol. 42, p. 365, 2003.

The following path gives the location of the Reaction Engineering Lab model:

Model Library path: Combustion/nox_reduction

The following path shows the location of the COMSOL Multiphysics model:

Model Library path:

Chemical_Engineering_Module/Transport_and_Reactions/nox_reduction

Modeling Using the COMSOL Reaction Engineering Lab

MODEL NAVIGATOR

- 1 Start COMSOL Multiphysics.
- 2 In the **Model Navigator**, go to the **Space dimension** list and select **Axial symmetry (2D)**.
- 3 Click **OK**.
The main user interface of COMSOL Multiphysics opens up.
- 4 From the **File** menu, select **Reaction Engineering Lab**.
The main user interface of COMSOL Reaction Engineering Lab opens up.
- 5 Click the **COMSOL Reaction Engineering Lab** window.

OPTIONS AND SETTINGS

- 1 Click the **Model Settings** button on the Main toolbar.
- 2 From the **Reactor type** list, select **Plug-flow**.
- 3 Select the **Calculate thermodynamic properties** check box.
- 4 Select the **Calculate species transport properties** check box.
- 5 On the **General** page, type 523 in the **Temperature** edit field.
- 6 On the **Mass Balance** page, type $v_{av} \cdot A$ in the **Volumetric flow rate** edit field.
- 7 Click **Close**.

REACTIONS INTERFACE

- 1 Click the **Reaction Settings** button on the Main toolbar.
- 2 Make sure the **Reactions** page is active. Create two entries in the **Reaction selection** list by clicking the **New** button twice.

- 3 Enter the following reaction formulas by first selecting the appropriate row in the **Reaction selection** list and then entering the corresponding text in the **Formula** edit field:

REACTION ID #	REACTION FORMULA
1	$4\text{NO} + 4\text{NH}_3 + \text{O}_2 \Rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$
2	$4\text{NH}_3 + 3\text{O}_2 \Rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}$

- 4 Select the first row in the **Reaction selection** list.
- 5 Select the **Use Arrhenius expressions** check box.
- 6 Type $1\text{e}6$ in the **A** edit field and $60\text{e}3$ in the **E** edit field.
- 7 Modify the predefined reaction rate according to Equation 4-55 on page 235 by typing $k_f_1 * c_{\text{NO}} * a * c_{\text{NH}_3} / (1 + a * c_{\text{NH}_3})$ in the **r** edit field.
You define the expression for **a** later on.
- 8 Select the second row in the **Reaction selection** list.
- 9 Select the **Use Arrhenius expressions** check box.
- 10 Type $6.8\text{e}7$ in the **A** edit field and $85\text{e}3$ in the **E** edit field.
- 11 Modify the predefined reaction rate according to Equation 4-58 on page 235 by typing $k_f_2 * c_{\text{NH}_3}$ in the **r** edit field.

SPECIES INTERFACE

- 1 Click the **Species** tab.
- 2 Check that the **Species selection** list has the five entries expected from entering the reaction formulas just given.
- 3 Click the **General** tab. Select the appropriate entry in the **Species selection** list and then enter the corresponding value for the **Molecular weight**:

SPECIES NAME	M [kg/mol]
NO	$30\text{e}-3$
NH3	$17\text{e}-3$
O2	$32\text{e}-3$
N2	$28\text{e}-3$
H2O	$18\text{e}-3$

- 4 Select **N2** from the **Species selection** list and choose **Solvent** from the **Type** list.

This selection is appropriate when a species is the main component of a reaction mixture. Setting a species as a **Solvent** removes its mass balance (the concentration is assumed to be constant). Furthermore, the thermodynamic and transport properties of the reacting mixture are based on the properties of the solvent species.

- 5 Click the **Feed Stream** tab. Select the appropriate entry in the **Species selection** list and then enter the corresponding value for the **Inlet molar flow**:

SPECIES NAME	F ₀ [mol/s]
NO	3.07e -8
NH3	3.96e -8
O2	6.67e -6
N2	7.23e -5
H2O	8.78e -6

- 6 Select **File>Import>CHEMKIN Transport Input File** and browse to the file `nox_reduction_transport.txt` then click **Import**.

This imports the Lennard-Jones parameters required to set up expressions for the fluid viscosity and species diffusivities.

- 7 Click the **Transport** page and verify that the σ , ϵ/k_B , and μ edit fields have been updated with the appropriate parameter values.

As an alternative to reading in the values from file, you can type in the appropriate values in the σ , ϵ/k_B , and μ edit fields:

SPECIES NAME	σ [m]	ϵ/k_B [K]	μ [D]
NO	3.62	97.5	0
NH3	2.90	558.3	1.47
O2	3.47	106.7	0
N2	3.80	71.4	0
H2O	2.64	809.1	1.88

- 8 Click **Close**.

OPTIONS AND SETTINGS

1 Choose **Model>Constants** and type in the following entries:

NAME	EXPRESSION	DESCRIPTION
A0	2.68e-17	Frequency factor (1/s)
E0	-243e3	Activation energy (J/mol)
rad	2e-3	Channel radius (m)
A	$\pi \cdot \text{rad}^2$	Channel cross section
v_av	0.3	Average gas velocity (m/s)

2 Click **OK**.

3 Choose **Model>Expressions** and type in the following entries:

NAME	EXPRESSION	DESCRIPTION
a	$A0 \cdot \exp(-E0 / (Rg \cdot T))$	Arrhenius expression
S	r_1 / r_2	Selectivity parameter
z	t / A	Axial distance from inlet

4 Click **OK**.

COMPUTING THE SOLUTION

1 Click the **Solver Parameters** button on the Main toolbar.

2 In the **Reactor volumes** edit field, type $\pi \cdot 0.002^2 \cdot 0.36$, that is, the volume of the monolith channel.

3 Set the **Relative tolerance** to $1e-9$ and the **Absolute tolerance** to $1e-10$.

4 Set the **Steady-state relative tolerance** to $1e-12$.

5 Click **OK**.

6 Click the **Solve** button on the Main toolbar.

POSTPROCESSING AND VISUALIZATION

The concentration transients of all species are plotted by default. Reproduce Figure 4-27 on page 240 and the plug-flow graph of Figure 4-31 on page 243 with the following steps:

1 Click the **Plot Parameters** button on the Main toolbar.

2 Remove all entries from the **Quantities to plot** list by clicking the **<<** button.

3 In the **Expression** edit field type c_{NO} , then click the **>** button.

- 4 In the **x-axis data** area, click first the lower option button and then the **Expression** button. In the **Expression** edit field, type z , then click **OK**.
- 5 From the **Plot in** list, select **New figure**. Click **Apply** to generate the first part of Figure 4-31 in a separate figure window; leave this window open.
- 6 In the **Expression** edit field type c_{NH_3} , then click the **>** button.
- 7 In the **Expression** edit field type $S/1000$, then click the **>** button.
- 8 From the **Plot in** list, select **Main axes**, then click **OK** to generate the plot in Figure 4-27.

Now move on to see how temperature affects the initial reaction rates.

OPTIONS AND SETTINGS

- 1 Click the **Model Settings** button on the Main toolbar.
- 2 On the **General** page, type $450+300*t$ in the **Temperature** edit field.
As you later set the simulation time to 1 second, this imposes a temperature profile increasing linearly from 450 K at $t = 0$ to 750 K at $t = 1$ s.
- 3 Click **Close**.

SPECIES INTERFACE

- 1 Click the **Reaction Settings** button on the Main toolbar.
- 2 Click the **Species** tab.
- 3 Click the **General** tab.
- 4 Select **NO** from the **Species selection** list, then select the **Lock concentration/activity** check box.
- 5 Type $F0_{\text{NO}}/(v_{\text{av}}*A)$ in the **Initial concentration** edit field.
Note how you can use the default variable name for the inlet molar flow and divide it by the volumetric flow to create an expression for the initial concentration.
- 6 Select **NH₃** from the **Species selection** list and select the **Lock concentration/activity** check box.
- 7 Type $F0_{\text{NH}_3}/(v_{\text{av}}*A)$ in the **Initial concentration** edit field.
- 8 Click **Close**.

By locking the concentrations of the species affecting the reaction rates r_1 and r_2 you can evaluate the initial rates as functions of temperature.

COMPUTING THE SOLUTION

- 1 Click the **Solver Parameters** button on the Main toolbar.
- 2 In the **Reactor volumes** edit field type 1.
- 3 Click **OK**.
- 4 Click the **Solve** button on the Main toolbar.

POSTPROCESSING AND VISUALIZATION

Reproduce Figure 4-28 on page 241 with the following steps:

- 1 Click the **Plot Parameters** button on the Main toolbar.
- 2 Remove all entries from the **Quantities to plot** list by clicking the << button.
- 3 In the **Predefined quantities** list, select Reaction rate 1, then click the > button.
- 4 In the **Predefined quantities** list, select Reaction rate 2, then click the > button.
- 5 Click the **Expression** option button in the **x-axis data** area.
- 6 Click the **Expression** button and type T in the edit field. Click **OK**.
- 7 Click **OK** to close the **Plot Parameters** dialog box and generate the plot.

Now restore some of the settings in the Reaction Engineering Lab before moving on to export the reaction model to COMSOL Multiphysics.

OPTIONS AND SETTINGS

- 1 Click the **Model Settings** button on the Main toolbar.
- 2 Type 523 in the **Temperature** edit field.
- 3 Click **Close**.

SPECIES INTERFACE

- 1 Click the **Reaction Settings** button on the Main toolbar.
- 2 Click the **Species** tab.
- 3 Select **NO** from the **Species selection** list. Clear the **Lock concentration/activity** check box and type 0 in the **Initial concentration** edit field.
- 4 Select **NH3** from the **Species selection** list. Clear the **Lock concentration/activity** check box and type 0 in the **Initial concentration** edit field.
- 5 Click **Close**.

EXPORT SETTINGS

- 1 Click the **Export to COMSOL Multiphysics** button on the Main toolbar.

- 2 The **Export to COMSOL Multiphysics** dialog box appears.
- 3 Go to the **Export mass balance** area, and in the **Application mode** list select **Convection and Diffusion: New**.
- 4 In the **Group name** edit field type mass.
- 5 Move to the **Export energy balance** area and clear the check box in the upper left corner.
- 6 Go to the **Export momentum balance** area, and in the **Application mode** list select **Incompressible Navier-Stokes: New**.
- 7 In the **Group name** edit field type momentum.
- 8 Click the **Export** button at the bottom of the dialog box.

Modeling Using COMSOL Multiphysics

It is now time to investigate the chemistry taking place in a space-dependent model, in this case in a channel of a honeycomb reactor. After drawing the model geometry you use the application modes (predefined balance equations) of the Chemical Engineering Module to set up and solve mass and momentum balances.

Click the **COMSOL Multiphysics** window.

GEOMETRY MODELING

Remember that in the axisymmetry modes, the symmetry axis is at r (or x) = 0, and that the geometry is built to the right of the axis.

- 1 Press the Shift key and click the **Rectangle/Square** button.
- 2 Type the following values in the corresponding edit fields for the rectangle dimensions:

SIZE		POSITION	
Width	2e - 3	r	0
Height	400e - 3	z	0

- 3 Click **OK**.
- 4 Press the Shift key again and click the **Rectangle/Square** button.

- 5 Type the following values in the corresponding edit fields for the rectangle dimensions:

SIZE		POSITION	
Width	1e-3	r	2e-3
Height	360e-3	z	20e-3

- 6 Click **OK**.

Now zoom in on this very narrow geometry.

- 7 Choose **Option>Axes/Grid Settings**.

- 8 Clear the **Axis equal** check box. In the **r-z limits** area, enter the following settings:

PROPERTY	VALUE
r min	-0.003
r max	0.005
z min	-0.01
z max	0.41

- 9 Click **OK**.

OPTIONS AND SETTINGS

Constants

- 1 From the **Options** menu, select **Constants**.
- 2 Enter the following parameter names and values in the **Constants** dialog box:

NAME	EXPRESSION	DESCRIPTION
v_av	0.3[m/s]	Average inlet velocity
p_ref	101325[Pa]	Pressure
eps_p	0.4	Porosity
k	1e-8[m^2]	Permeability
k_eff	0.25	Effectiveness factor
c_NO_in	8.16e-3[mol/m^3]	Inlet concentration
c_NH3_in	1.05e-2[mol/m^3]	Inlet concentration
c_O2_in	1.77[mol/m^3]	Inlet concentration
c_H2O_in	2.33[mol/m^3]	Inlet concentration

- 3 Click **OK**.

Projection Coupling Variables

To enable a comparison between the plug-flow and channel models, it is of interest to calculate the NO concentration averaged over the channel cross section as a function of the axial coordinate along the reactor channel. This quantity is given by the integral

$$c_{\text{NO,mean}}(z) = \frac{1}{A} \int_{\Omega} c(\mathbf{x}) dA = \frac{2}{R^2} \int_0^R c_{\text{NO}}(r, z) r dr$$

To make it available for postprocessing, define a projection coupling variable, `co_NO_mean`, according to the following instructions (for a description of projection coupling variables, see the section “Projection Coupling Variables” on page 270 of the *COMSOL Multiphysics User’s Guide*).

- 1 From the **Options** menu, select **Projection Coupling Variables>Subdomain Variables**.
- 2 On the **Source** page, select Subdomain 1, then enter the following data on the first row of the table:

NAME	EXPRESSION	INTEGRATION ORDER
c_NO_mean	2 / (0.002^2) * r * c_NO	4

- 3 Click the **General transformation** option button. In the **Source transformation** area, set **x** to **z** and **y** to **r**.
- 4 Click the **Destination** tab. From the **Level** list, select **Boundary**.
- 5 Select Boundary 5, then select the **Use selected boundaries as destination** check box.
- 6 In the **Destination transformation** area, set **x** to **z**, then click **OK**.

PHYSICS SETTINGS

Subdomain Settings—Navier-Stokes Application Mode

- 1 From the **Multiphysics** menu, select **Incompressible Navier-Stokes (chns)**.
- 2 From the **Physics** menu, select **Properties**. From the **Analysis type** list, select **Stationary**. Click **OK**.
- 3 From the **Physics** menu, select **Subdomain Settings**.
- 4 Select Subdomains 1 and 2 from the **Subdomain selection** list by pressing Ctrl+A and clicking in the list.
- 5 From the **Group** list, select **momentum**.

Note how the **Density** and **Dynamic viscosity** edit fields are automatically filled in as a result of exporting the group **momentum** from the Reaction Engineering Lab.

- 6 Click the **Init** tab.
- 7 Type p_{ref} in the **Pressure** edit field.
- 8 Go back to the **Physics** tab.
- 9 Select Subdomain 2 (the porous-medium subdomain) from the **Subdomain selection** list.
- 10 Select the **Flow in porous media** check box.
- 11 Type ϵ_p in the **Porosity** edit field and k in the **Permeability** edit field.
- 12 Click **OK**.

Boundary Conditions—Navier-Stokes Application Mode

- 1 From the **Physics** menu, select **Boundary Settings**.
- 2 Enter the boundary conditions according to the following table:

SETTINGS	BOUNDARY 1	BOUNDARY 2	BOUNDARY 3	ALL OTHERS
Boundary type	Symmetry boundary	Inlet	Outlet	Wall
Boundary condition	Axial symmetry	Velocity	Pressure, no viscous stress	No slip
u_0		0		
v_0		$v_{av} \cdot 2 \cdot (1 - s^2)$		
p_0			p_{ref}	

Here you set up a parabolic inlet-velocity profile at the channel inlet. The velocity expression uses the built-in parameterization variable s that is available on boundaries in 2D. The value of s runs from 0 to 1 along any given boundary.

- 3 Click **OK**.

Subdomain Settings—Convection and Diffusion

- 1 From the **Multiphysics** menu, select **Convection and Diffusion (chcd)**.
- 2 From the **Physics** menu, select **Properties**. From the **Analysis type** list, select **Stationary**. Click **OK**.
- 3 From the **Physics** menu, select **Subdomain Settings**.
- 4 Select Subdomains 1 and 2 from the **Subdomain selection list** by pressing Ctrl+A and clicking in the list.
- 5 Select **mass** from the **Group** list.

Note how the **Diffusion coefficient** and **Reaction rate** edit fields are automatically filled in as a result of exporting the group **mass** from the Reaction Engineering Lab.

- 6 Click the **c_NO** tab.
- 7 Type *u* in the **r-velocity** edit field and *v* in the **z-velocity** edit field.
- 8 Repeat Steps 6 and 7 for the remaining species (**c_NH3**, **c_O2**, and **c_H2O**) by clicking their respective tabs.
- 9 Select Subdomain 1 from the **Subdomain selection** list.
- 10 Click the **c_NO** tab.
- 11 As no reaction takes place in the gas phase, type 0 in the **Reaction rate** edit field.
- 12 Repeat Step 11 for the remaining species (**c_NH3**, **c_O2**, and **c_H2O**) by clicking their respective tabs.
- 13 Select Subdomain 2 from the **Subdomain selection** list.

You must somewhat modify the gas-phase diffusivities exported from the Reaction Engineering Lab to represent the corresponding diffusivities in the porous domain. The effective diffusivity ($D_{i,\text{eff}}$) in a porous material is related to the gas-phase diffusivity (D_i) by

$$D_{i,\text{eff}} = \frac{\phi \sigma D_i}{\tau}$$

where, ϕ is the porosity, σ gives the constriction factor, and τ equals the tortuosity. Here, the material properties are grouped into the factor $k_{\text{eff}} = \phi \sigma / \tau$.

- 14 Click the **c_NO** tab.
- 15 In the **Diffusion coefficient** edit field, modify the existing expression by typing **k_eff*** at the beginning of the expression, then click **Apply**.
- 16 Repeat Step 15 for the remaining species (**c_NH3**, **c_O2**, and **c_H2O**) by clicking their respective tabs.
- 17 Click **OK**.

Boundary Conditions—Convection and Diffusion

- 1 From the **Physics** menu, select **Boundary Settings**.
- 2 Enter the boundary conditions for each of the species **c_NO**, **c_NH3**, **c_O2**, and **c_H2O** according to the following table:

SETTINGS	BOUNDARY 1	BOUNDARY 2	BOUNDARY 3	ALL OTHERS
Type	Axial symmetry	Concentration	Convective flux	Insulation/Symmetry
c_NO ₀		c_NO_in		
c_NH3 ₀		c_NH3_in		

SETTINGS	BOUNDARY 1	BOUNDARY 2	BOUNDARY 3	ALL OTHERS
c_O2 ₀		c_O2_in		
c_H2O ₀		c_H2O_in		

3 Click **OK**.

MESH GENERATION

Because projection coupling variables require simplex mesh elements, you must use a triangular mesh.

- 1 From the **Mesh** menu, choose **Free Mesh Parameters**.
- 2 On the **Global** page, select **Extremely fine** from the **Predefined mesh sizes** list.
To fully resolve this model requires a very dense mesh; the above setting results in a model size of roughly 386,000 degrees of freedom. If you want to reduce memory consumption and solution time at the cost of obtaining a solution which is numerically slightly inaccurate, you can select the mesh size **Extra fine** instead.
- 3 Click the **Advanced** tab. Set the **r-direction scale factor** to 100. This setting is necessary to obtain a sufficient mesh resolution in the radial direction.
- 4 Click the **Remesh** button, then click **OK**.

COMPUTING THE SOLUTION

It is not necessary to solve both the momentum and mass balances simultaneously because the fluid flow is independent of the concentration. Therefore, to save time and computer memory, first solve the momentum balances and then solve the mass balances on the existing flow profile.

- 1 From the **Solve** menu, select **Solver Parameters**.
- 2 From the **Solver** list, select **Stationary**.
- 3 Go to the **Advanced** page.
- 4 In the **Type of scaling** list, select **None**.
- 5 Click **OK**.
- 6 From the **Solve** menu, select **Solver Manager**.
- 7 On the **Solve For** page, select **Incompressible Navier-Stokes** in the **Solve for variables** tree.
- 8 Click the **Solve** button. The solution time is around 2 minutes.
- 9 On the **Initial Value** page click the **Store Solution** button.
- 10 Click the **Stored solution** option button in the **Initial value** area.

- 11 Return to the **Solve For** page and select **Convection and Diffusion**.
- 12 Click **OK**.
- 13 Click the **Solve** button on the Main toolbar. The solution time is roughly 4 minutes.

POSTPROCESSING AND VISUALIZATION

The default plot shows the concentration of NO across the modeling domain, as seen in Figure 4-30 on page 242.

The following steps reproduce Figure 4-29 on page 241:

- 1 From the **Postprocessing** menu, open the **Cross-Section Plot Parameters** dialog box.
- 2 On the **General** page, clear the **Display cross-section in main axes** check box.
- 3 On the **Line/Extrusion** page, select **Incompressible Navier-Stokes (chns)>z-velocity** from the **Predefined quantities** list.
- 4 In the **x-axis data** area, click first the lower option button and then the **Expression** button to open the **X-Axis Data** dialog box. Type **r** in the **Expression** edit field, then select **mm** from the **Unit** list. Click **OK** to close the dialog box.
- 5 In the **Cross-Section Plot Parameters** dialog box, go to the **Cross-section line data** area.
- 6 Type **0** in the **r0** edit field and **0.003** in the **r1** edit field.
- 7 Type **0.2** in both the **z0** and **z1** edit fields.
- 8 Click **OK** to close the dialog box and generate the plot.

To finish the plot in Figure 4-31 on page 243, follow these instructions.

- 1 From the **Postprocessing** menu, open the **Domain Plot Parameters** dialog box.
- 2 On the **General** page, select the **Keep current plot** check box. From the **Plot in** list, select the figure window in which you plotted the first graph (**Figure 1**, unless you had any open figure windows from previous modeling sessions).
- 3 Go to the **Line/Extrusion** page and select Boundary 5. In the **y-axis data** area, type **c_NO_mean** in the **Expression** edit field.
- 4 Click the **Line Settings** button. From the **Line color** list, select **Color**, then click the **Color** button. In the **Line Color** dialog box, select a green color, then click **OK**. From the **Line style** list, select **Dashed line**, then click **OK** to close the **Line Settings** dialog box.
- 5 Click **OK** to close the **Domain Plot Parameters** dialog box and generate the plot.
- 6 Click the **Edit Plot** toolbar button in the figure window, then use the **Edit Plot** dialog box to edit plot title, axis labels, and legends.

To calculate the conversion of NO to N₂, perform an integration of the mass flux over the inlet and outlet:

- 1 From the **Postprocessing** menu, select **Boundary Integration**.
- 2 Select Boundary 2 (the inlet), and then in the **Predefined quantities** list select **Convection and Diffusion>Normal total flux, c_NO**.
- 3 Select the check box beside **Compute surface integral (for axisymmetric modes)**.
- 4 Click **Apply**.
- 5 Select Boundary 3 (the outlet).
- 6 Click **OK**.

The values from the flux integrations appear in the message log at the bottom of the user interface. The inlet integration yields $-3.08 \cdot 10^{-8}$ mol/s, while outlet integration yields $3.5 \cdot 10^{-9}$ mol/s. The flux is defined as leaving the geometry domain, hence the minus sign at the inlet. The conversion of NO becomes

$$\frac{3.08 - 0.35}{3.08} = 0.89$$

Homogeneous Charge Compression Ignition of Methane

Introduction

Homogeneous Charge Compression Ignition (HCCI) engines are being considered as an alternative to traditional spark- and compression-ignition engines. As the name implies, a homogeneous fuel/oxidant mixture is autoignited by compression with simultaneous combustion occurring throughout the cylinder volume. Combustion temperatures under lean burn operation are relatively low, resulting in low levels of NO_x emission. Furthermore, the fuel's homogeneous nature as well as the combustion process itself lead to low levels of particulate matter being produced.

Although HCCI combustion shows much promise, the method also suffers from a number of recurring problems, one of the more important being ignition timing. The following model examines the HCCI of methane, investigating ignition trends as a function of initial temperature, initial pressure, and fuel additives.

This model solves the mass and energy balances describing the detailed combustion of methane in a variable-volume system. The large amount of kinetic and thermodynamic data required to set up the problem is readily made available by importing relevant files into the Reaction Engineering Lab.

Model Definition

It is difficult to form the uniform mixtures required for HCCI with conventional diesel fuel. Natural-gas fuels, on the other hand, readily produce homogeneous mixtures and have the potential to serve as HCCI fuels. This example considers the combustion of methane, as described by the GRI-3.0 mechanism, incorporating a detailed reaction mechanism of 53 species taking part in 325 reactions. The files describing the reaction kinetics and thermodynamics of the GRI-3.0 mechanism are available on the Internet (Ref. 1), and you can import these files directly into the Reaction Engineering Lab.

VARIABLE VOLUME REACTOR

This model represents the combustion cylinder with a perfectly mixed batch system of variable volume, a reactor type that is predefined in the Reaction Engineering Lab.

Figure 4-32 shows a drawing of an engine cylinder, and it points out parameters relevant for calculating the instantaneous cylinder volume.

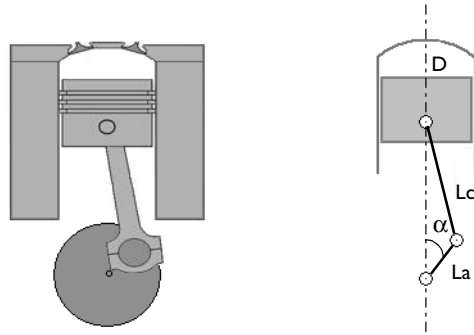


Figure 4-32: The volume of a combustion cylinder can be expressed as a function of time with the slider-crank relationship. This diagram shows the key geometric parameters. L_a is the length of the crank arm, L_c gives the length of the connecting rod, D equals the cylinder diameter, and α is the crank angle.

The volume change as a function of time is described by the slider-crank equation:

$$\frac{V}{V_c} = 1 + \frac{(CR-1)}{2} [R + 1 - \cos \alpha - \sqrt{R^2 - (\sin \alpha)^2}] \quad (4-75)$$

where, V is the cylinder volume (m^3), V_c gives the clearance volume (m^3), CR equals the compression ratio, and R denotes the ratio of the connecting rod to the crank arm (L_c/L_a). Further, α is the crank angle (rad), which is also a function of time

$$\alpha = \frac{2\pi N}{60} t \quad (4-76)$$

where N is the engine speed in rpm, and t is the time (s).

The engine specifications used in the model are:

ENGINE SPECIFICATION	VARIABLE NAME	VALUE
Bore	D	13 cm
Stroke	S	16 cm
Connecting rod	L_c	26.93 cm
Crank arm	L_a	8 cm
Engine speed	N	1500 rpm
Compression ratio	CR	15

Equation 4-77 includes the clearance volume, V_c , which is calculated from

$$V_c = \frac{V_s}{(CR - 1)} \quad (4-77)$$

V_s is the volume swept by the piston during a cycle from the equation

$$V_s = \frac{\pi D^2}{4} S \quad (4-78)$$

Figure 4-33 shows the calculated cylinder volume as a function of the crank angle. The piston is initially at bottom dead center (BDC), corresponding to a crank angle of -180 degrees.

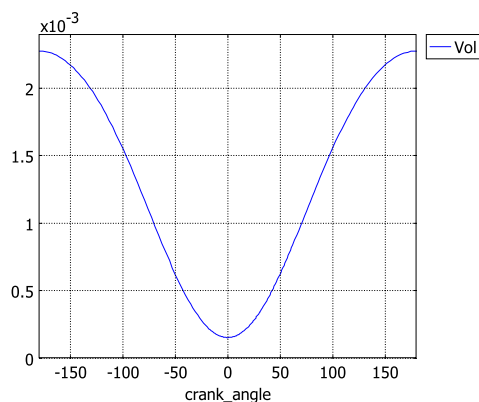


Figure 4-33: Cylinder volume as function of crank angle. The crank angle is defined as being zero at top dead center (TDC).

MASS AND ENERGY BALANCES

The mass balances describing a perfectly mixed reactor with variable volume are summarized by

$$\frac{d(Vc_i)}{dt} = VR_i \quad (4-79)$$

where c_i represents the species concentration (mol/m^3), and R_i denotes the species rate expression ($\text{mol}/(\text{m}^3 \cdot \text{s})$).

For an ideal gas mixture, the reactor energy balance is

$$V_r \sum_i c_i C_{p,i} \frac{dT}{dt} = \dot{Q} + \dot{Q}_{\text{ext}} + V_r \frac{dp}{dt} \quad (4-80)$$

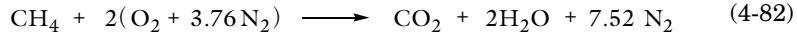
where $C_{p,i}$ is the species molar heat capacity (J/(mol·K)), T is the temperature (K), and p gives the pressure (Pa). In this equation, \dot{Q} is the heat due to chemical reaction (J/s)

$$\dot{Q} = -V_r \sum_j H_j r_j \quad (4-81)$$

where H_j is the enthalpy of reaction (J/(mol·K)), and r_j equals the reaction rate (mol/(m³·s)). \dot{Q}_{ext} denotes heat added to the system (J/s). The model being described assumes adiabatic conditions, that is, $\dot{Q}_{\text{ext}} = 0$.

The kinetic and thermodynamic data for methane combustion is available in the form of data input files. Once you have imported them into the Reaction Engineering Lab, the software automatically sets up the mass and energy balances detailed in Equation 4-79 and Equation 4-80.

To complete the model setup, all that remains is to define the initial conditions. In this model, methane is combusted under lean conditions, that is, supplying more than the stoichiometric amount of oxidizer. The stoichiometric requirement of the oxidizer (air) to combust methane is found from the overall reaction:



Assuming that the composition of air is 21% oxygen and 79% nitrogen, the stoichiometric air-fuel ratio is

$$(A/F)_{\text{stoic}} = \left(\frac{m_{\text{air}}}{m_{\text{fuel}}} \right)_{\text{stoic}} = \frac{4.76 \cdot 2 \cdot M_{\text{air}}}{1 \cdot M_{\text{fuel}}} \quad (4-83)$$

The equivalence ratio relates the actual air-fuel ratio to the stoichiometric requirements

$$\Phi = \frac{(A/F)_{\text{stoic}}}{(A/F)} \quad (4-84)$$

This model sets the equivalence ratio to $\Phi = 0.5$.

From Equation 4-83 and Equation 4-84 you can calculate the molar fraction of fuel in the reacting mixture as

$$x_{\text{fuel}} = \frac{1}{4.76 \cdot 2 / \Phi + 1} \quad (4-85)$$

and subsequently the initial concentration is

$$c_{\text{fuel}} = \frac{x_{\text{fuel}} p_{\text{init}}}{RgT_{\text{init}}} \quad (4-86)$$

The initial pressure and the initial temperature are variable model parameters.

Results

Figure 4-34 shows the cylinder pressure as a function of time when a methane-air mixture is compressed and ignites. The piston starts at bottom dead center (BDC) and reaches top dead center (TDC) after 0.02 s. At BDC the pressure is set to $1.5 \cdot 10^5$ Pa, Φ is 0.5, and the compression ratio is $\text{CR} = 15$. The initial temperature is varied from 400 K to 800 K.

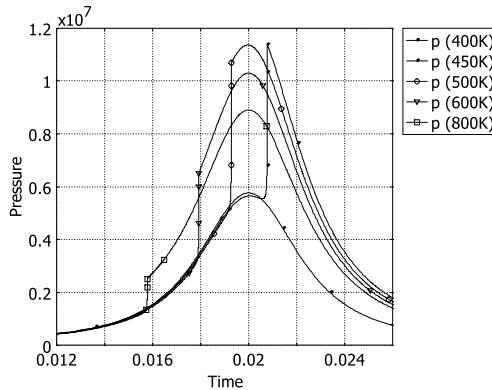


Figure 4-34: Pressure traces illustrating the compression and ignition of fuel in an engine cylinder. The initial temperature varies between 400 K and 800 K.

Consistent with literature results, methane does not ignite at an initial temperature of 400K (Ref. 2). Furthermore, the induction delay decreases with increasing initial temperature. The induction delay time can be evaluated from the pressure gradient. For instance, the induction delay is 0.0193 s when $T_{\text{init}} = 500$ K.

Figure 4-35 illustrates the pressure traces as the initial pressure varies from $1 \cdot 10^5$ Pa to $3 \cdot 10^5$ Pa. The initial temperature is 500 K. An increase in pressure means an increase

in the species concentrations in the fuel-air mixture, resulting in the expected advance in ignition times.

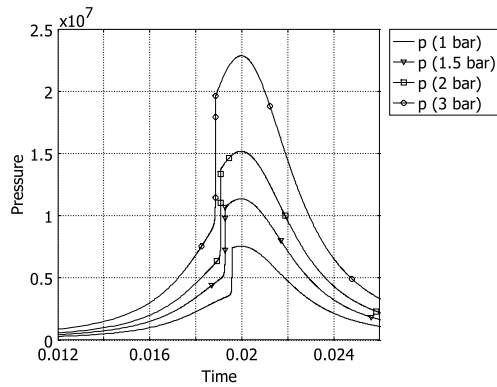


Figure 4-35: Increased initial gas pressure advances ignition times.

As mentioned previously, a significant challenge to the realization of HCCI engines is ignition control. In this regard, combustion at TDC has been suggested as the optimum timing (Ref. 3). The results just discussed show that the inlet temperature of the fuel-air mixture is a potential tuning parameter for ignition. However, relatively high inlet temperatures are often required for proper timing. This adversely affects engine performance because the trapped mass as well as the volumetric efficiency decreases. An alternative that facilitates ignition is to mix small amounts of additives into the fuel-air mixture (Ref. 4). These additives chemically activate the reaction mixture even at relatively low temperatures. This approach alleviates the requirements of high intake temperatures. Figure 4-36 shows how small amounts of formaldehyde

(CH₂O) cause ignition at an initial temperature of 400 K, a temperature insufficient to induce combustion with a pure methane fuel.

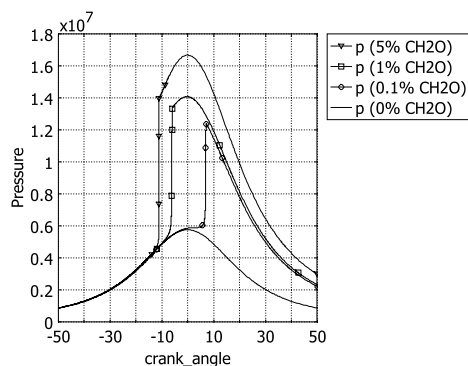
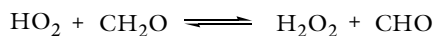
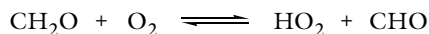


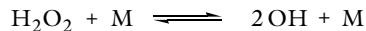
Figure 4-36: Small amounts of formaldehyde stimulate ignition of the fuel-air mixture.

The increased reactivity observed in the presence of CH₂O is explained by the opening of a new chemical pathway leading to the formation of hydroxyl radicals. Specifically,

CH₂O reacts with O₂ to produce H₂O₂:



H₂O₂, in turn, decomposes to reactive OH radicals, which subsequently react violently with the fuel molecules to cause ignition:



The results in the following graphs show the species molar fractions of CH₂O, HO₂, H₂O₂, and OH during the combustion of methane. Figure 4-37 shows molar fraction plots for the case when 0.13% CH₂O is added to the fuel; Figure 4-38 is the equivalent species plots for the case when pure methane is combusted. In each case conditions

have been tuned to produce ignition near TDC so as to provide a reference point for comparing the species concentrations.

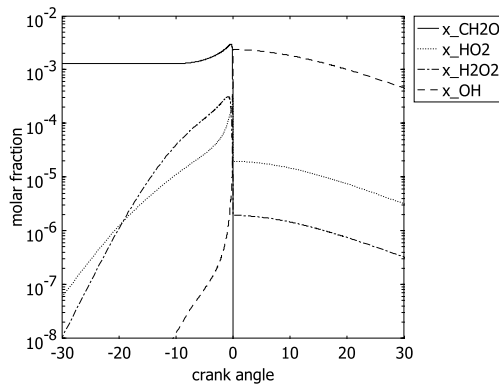


Figure 4-37: Selected species molar fractions as a function of crank angle. 0.26 molar percent CH_2O is added to the reacting mixture, which is initially at 400 K and 1.5 bar.

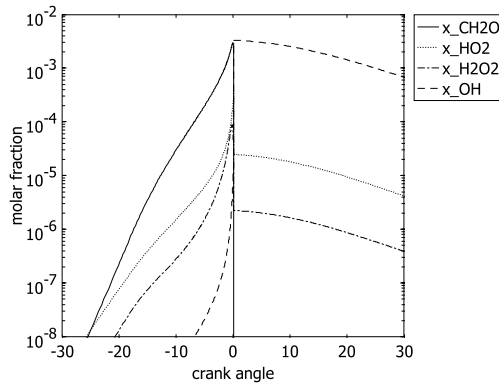


Figure 4-38: Selected species molar fraction as a function of crank angle. Only methane is combusted. The initial temperature is 469 K and the initial pressure 1.5 bar.

The implications of the CH_2O reaction path just outlined are directly visible by comparing Figure 4-37 and Figure 4-38; CH_2O stimulates the production of HO_2 and H_2O_2 that in turn produce OH radicals in amounts critical to fuel ignition.

References

1. G.P. Smith, D.M. Golden, M. Frenklach, N.W. Moriarty, B. Eiteneer, M. Goldenberg, C.T. Bowman, R.K. Hanson, S. Song, W.C. Gardiner, Jr., V. V. Lissianski, and Z. Qin, GRI-MECH 3.0, http://www.me.berkeley.edu/gri_mech/.
2. S.B. Fiveland and D.N. Assanis, *SAE Paper 2000-01-0332*, 2000.
3. D.L. Flowers, S.M. Aceves, C.K. Westbrook, J.R. Smith, and R.W. Dibble, *J. Eng. Gas Turbine Power*, vol. 123, p. 433, 2001.
4. M.H. Morsy, *Fuel*, vol. 86, p. 533, 2007.

Model Library path: Combustion/compression_ignition

Modeling Using the COMSOL Reaction Engineering Lab

The kinetic and thermodynamic data required for this model are available on the Internet. Find the GRI-Mech 3.0 input files at (Ref. 1):

http://www.me.berkeley.edu/gri_mech/version30/text30.html.

Download the reaction mechanism and rate coefficient file (`grimech30.dat`), as well as thermodynamic data file (`thermo30.dat`) and store them on your computer.

MODEL NAVIGATOR

- 1 Start the COMSOL Reaction Engineering Lab.
- 2 In the **Model Navigator** click the **New** button.

Proceed to import the chemical kinetics and thermodynamics data files.

- 1 Select **File>Import>CHEMKIN Kinetics Input File**.
Importing a kinetics file is equivalent to setting up a new reaction model. The software therefore asks you to save any current model you are working with.
- 2 Browse to the folder containing the appropriate file (`grimech30.dat`) and click the **Import** button.
- 3 Select **File>Import>CHEMKIN Thermo Input File**.
- 4 Browse to the folder containing the appropriate file (`thermo30.dat`) and click the **Import** button.

OPTIONS AND SETTINGS

Start by setting up constants and expressions used in the model.

1 Select the menu item **Model>Constants**.

2 Type in the entries in the table below.

Alternatively, click the **Import Variables From File** button in the **Constants** dialog box, browse to the file `compression_ignition_const.txt` on your computer and click **Open**.

NAME	EXPRESSION	DESCRIPTION
T_init	400	Initial temperature at BDC
p_init	1.5e5	Initial pressure at BDC
La	0.08	Crank arm length
Lc	0.2693	Connecting rod length
S	0.16	Stroke
D	0.13	Bore diameter
CR	15	Compression ratio
N	1500	Engine rpm
ER	0.5	Equivalence ratio

3 Click **OK**.

4 Select **Model>Expressions**.

5 Type in the entries in the table below.

Alternatively, click the **Import Variables From File** button in the **Expressions** dialog box, browse to the file `compression_ignition_expr.txt` on your computer and click **Open**.

NAME	EXPRESSION	DESCRIPTION
Vol	$V_c * (1 + (CR - 1) / (2 * (R + 1 - \cos(\alpha) - \sqrt{R^2 - \sin(\alpha)^2})))$	Cylinder volume
V_s	$\pi * D^2 / 4 * S$	Swept volume
V_c	$V_s / (CR - 1)$	Clearance volume
alpha	$t * 2 * \pi * N / 60 - \pi$	Crank angle (rad)
crank_angle	$\alpha * 180 / \pi$	Crank angle (deg)
R	L_c / L_a	Length ratio
x_CH4	$1 / (4.76 * 2 / ER + 1)$	Initial CH4 mole fraction
x_O2	$0.21 * (1 - x_{CH4})$	Initial O2 mole fraction

NAME	EXPRESSION	DESCRIPTION
x_N2	$1 - x_{CH4} - x_{O2} - x_{CH2O}$	Initial N2 mole fraction
x_CH2O	0	Initial CH2O mole fraction
c_CH4_0	$x_{CH4} * p_{init} / (Rg * T_{init})$	Initial CH4 concentration
c_O2_0	$x_{O2} * p_{init} / (Rg * T_{init})$	Initial O2 concentration
c_N2_0	$x_{N2} * p_{init} / (Rg * T_{init})$	Initial N2 concentration
c_CH2O_0	$x_{CH2O} * p_{init} / (Rg * T_{init})$	Initial CH2O concentration

6 Click **OK**.

Continue with global model settings.

7 Click the **Model Settings** button on the Main toolbar.

8 Select **Batch** from the **Reactor type** list.

9 Select the **Include energy balance** check box.

10 Go to the **Mass Balance** page and type Vol in the **Reactor volume** edit field.

11 Go to the **Init** page and type T_init in the **Initial temperature** edit field.

12 Click **Close**.

SPECIES INTERFACE

1 Click the **Reaction Settings** button on the Main toolbar.

2 Click the **Species** tab.

3 On the **General** page select the appropriate entry in the **Species selection** list, then enter the corresponding value for the **Initial concentration** in the **c₀** edit field:

SPECIES NAME	c ₀
O2	c_O2_0
CH2O	c_CH2O_0
CH4	c_CH4_0
N2	c_N2_0

4 Click **Close**.

COMPUTING THE SOLUTION

1 Click the **Solver Parameters** button on the Main toolbar.

2 Go to the **Times** edit field and enter 0.04. This is the time required for one piston cycle.

3 Type 1e-8 in the **Relative tolerance** edit field.

- 4 Type $1\text{e-}9$ in the **Absolute tolerance** edit field.
- 5 Click **OK**.
- 6 Solve the problem by clicking the **Solve** button on the Main toolbar.

POSTPROCESSING AND VISUALIZATION

By default, the model plots the concentration transients of species with a nonzero initial concentration. Reproduce Figure 4-34 with the following steps:

- 1 Click the **Plot Parameters** button on the Main toolbar.
- 2 Remove all entries from the **Quantities to plot** list by clicking the **<<** button.
- 3 In the **Expression** edit field type p , then click the **Add Entered Expression (>)** button.
- 4 Click **Apply**.
- 5 Select the **Keep current plot** check box.
- 6 Click **OK**.
- 7 Select the menu item **Model>Constants**.
- 8 Set the initial temperature **T_init** to 450 and click **OK**.
- 9 Solve the problem again with the new initial temperature by pressing the **=** button.
- 10 Continue in the same manner to produce results for the initial temperatures 500 K, 600 K, and 800 K.
- 11 Click the **Edit Plot** button.
- 12 On the **Axis** page, clear the **x limits Auto** check box and type 0.012 and 0.026 in the left and right edit fields, respectively.
- 13 Type Pressure in the **y label** edit field.
- 14 Select the first **Line (p)** entry, type p (400K) in the **Legends** edit field, and select the **Show legend** check box.
- 15 Select the second **Line (p)** entry, type p (450K) in the **Legends** edit field, select the **Show legend** check box, and select **Point** from the **Line marker** list.
- 16 Repeat the above steps for the pressure plots corresponding to the initial temperatures 500 K, 600 K, and 800 K, using a different line marker for each line.
- 17 Click **OK** to close the **Edit Plot** window.

Reproduce Figure 4-36 with the following steps:

1 Select **Model>Constants** and type in the following; when done, click **OK**.

NAME	EXPRESSION	DESCRIPTION
T_init	400	Initial temperature

2 Select **Model>Expressions** and type in the following; when done, click **OK**.

NAME	EXPRESSION	DESCRIPTION
x_CH2O	0.05	Initial CH2O mole fraction

3 Click the **Plot Parameters** button on the Main toolbar.

4 Clear the **Keep current plot** check box.

5 Select the **Expression** option button in the **x-axis data** area.

6 Click the **Expression** button.

7 Type crank_angle in the **Expression** edit field, then click **OK**.

8 Click **Apply** in the **Plot Parameters** window.

9 Click the **Solve** button on the Main toolbar.

10 Go to the **Plot Parameters** window.

11 Select the **Keep current plot** check box.

12 Click **OK** to close the **Plot Parameters** window.

13 Select the menu item **Model>Expressions** and set the initial mole fraction of formaldehyde by setting **x_CH2O** to 0.01.

14 Once again solve the problem with the new initial mole fraction by pressing the **=** button.

15 Continue in the same manner to produce results for the initial mole fraction 0.001 and 0.

16 Click the **Edit Plot** button.

17 On the **Axis** page, clear the **x limits** check box and type -50 and 50 in the left and right edit fields, respectively.

18 Type Pressure in the **y label** edit field.

19 Select the first **Line (p)** entry, type p (5% CH2O) in the **Legends** edit field, and select **Point** from the **Line marker** list.

20 Repeat steps the above steps for the pressure plots corresponding to the initial formaldehyde mole fractions of 0.01, 0.001, and 0.

Pesticide Transport and Reaction in Soil

Introduction

Aldicarb is a commercial pesticide, used on a variety of crops, including cotton, sugar beet, citrus fruits, potatoes, and beans. The general population may be exposed to aldicarb primarily through the ingestion of contaminated water and foods.

This example looks at the degradation kinetics of aldicarb and its toxic by-products, investigating both the degradation time-scale as well as the spatial concentration distribution of toxic components. In the first model the chemicals are contained in a water pond, treated as a perfectly mixed system. The second model tracks the detailed distribution of chemicals in soil as the pesticide leaches out of the pond and is transported in water through the ground.

The reaction kinetics describing the degradation pathways of aldicarb is exported to the Solute Transport application mode of the Earth Science Module. In COMSOL Multiphysics the solute transport is coupled to fluid flow as described by Richards' equation.

Note: This model requires the COMSOL Reaction Engineering Lab and the Earth Science Module.

Model Definition

Aldicarb degrades by transformation to the corresponding sulfoxide and the sulfone (both of which are toxic), and is detoxified by hydrolysis to oximes and nitriles. The chain of reactions is illustrated in Figure 4-39. The toxicity of a chemical species is indicated by its LD₅₀ value, signifying the dose (mg/kg) lethal to half of a test population of rats. As indicated, both the sulfoxide and sulfone analogues of aldicarb are also relatively toxic.

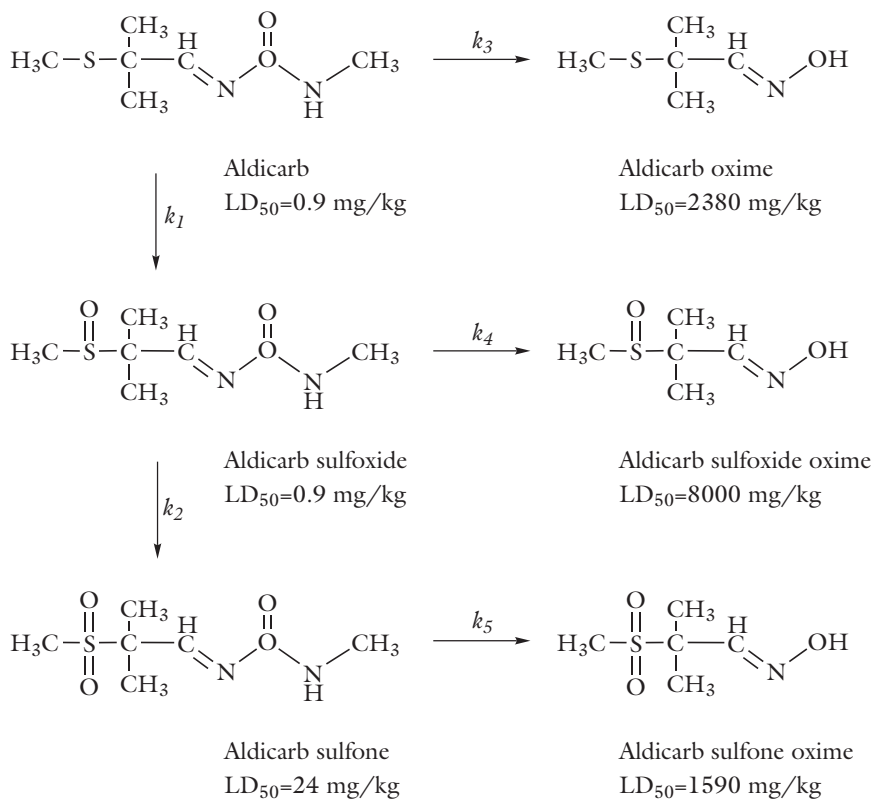


Figure 4-39: Reaction pathways of aldicarb degradation.

Each of the j unimolecular reactions outlined above have rate expressions of the form:

$$r_j = k_j c_i$$

Note that in this example the concentration unit is kg/m^3 and the rate constants are expressed in $1/\text{day}$.

PERFECTLY MIXED SYSTEM

The first model solves for the decomposition kinetics of aldicarb occurring in a water pond. The pond is treated as a closed and perfectly mixed system. The reaction

mechanism illustrated in Figure 4-39 translates into the following mass balance equations:

- For aldicarb (a)

$$\frac{dc_a}{dt} = -r_1 - r_3$$

- For aldicarb sulfoxide (asx)

$$\frac{dc_{asx}}{dt} = r_1 - r_2 - r_4$$

- For aldicarb sulfone (asn)

$$\frac{dc_{asn}}{dt} = r_2 - r_5$$

- For aldicarb oxime (ao)

$$\frac{dc_{ao}}{dt} = r_3$$

- For aldicarb sulfoxide oxime (asxo)

$$\frac{dc_{asxo}}{dt} = r_4$$

- For aldicarb sulfone oxime (asno)

$$\frac{dc_{asno}}{dt} = r_5$$

Solving this set of coupled ODEs outlined above provides information on the time scale of the degradation processes.

SPACE- AND TIME-DEPENDENT SYSTEM

In a more detailed model, you assume that aldicarb moves from the pond into relatively dry soil. In the soil, the aldicarb decomposes according to the mechanism illustrated in Figure 4-39. In addition, the pesticide and its decay products are transported by advection, dispersion, sorption, and volatilization.

Geometry

Water is ponded by a ring sitting on the ground. The soil is layered and rests on rocks. Water moves through the bottom of the ring into the soil. The water level in the ring is known. There is no flow through the vertical walls or the surface outside of the ring.

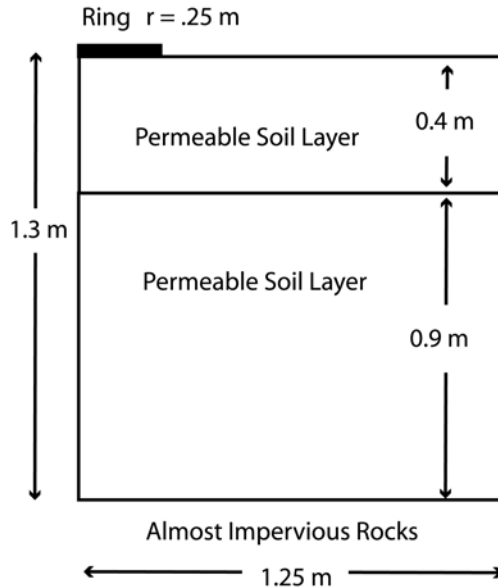


Figure 4-40: Geometry of the infiltration ring and soil column.

Aldicarb moves with water from the pond into the soil at a constant concentration. In the soil, the chemicals react and also sorb onto soil particles. Aldicarb and the aldicarb sulfone volatilize to the atmosphere. The sorption, biodegradation, and volatilization proceed in linear proportion to the aqueous concentrations. The soil is initially pristine with zero concentration of the involved chemicals. At the ground surface outside the ring, there is volatilization to the atmosphere for c_a and c_{asn} . The vertical axis is a line of symmetry. The other boundaries are posed such that the solutes can freely leave the soil column with the fluid flow. You can model the problem with 2D axisymmetry and track the solute transport for 10 days.

Fluid Flow

Richards' equation governs the saturated-unsaturated flow of water in soil (Ref. 1) and is implemented in the Richards' equation application mode:

$$[C + SeS]\frac{\partial H_p}{\partial t} + \nabla \cdot [-K_s k_r \nabla (H_p + D)] = Q_s$$

Here, C denotes specific moisture capacity (m^{-1}), Se is the effective saturation of the soil, S is a storage coefficient (m^{-1}), H_p represents the dependent variable pressure head (m), t is time (d), K equals the hydraulic conductivity function (m/d), D is the coordinate representing vertical elevation (for example, x , y , or z), and Q_s is a fluid source defined by volumetric flow rate per unit volume of soil (d^{-1}). In this problem, $S = \theta_s - \theta_r$, where θ_s and θ_r denote the volume fraction of fluid at saturation and after drainage, respectively.

You can find more detail on the Richards' Equation application mode in the Earth Science Module User's Guide.

Mass Transport

The governing equation for solute transport describes advection and dispersion of a sorbing, volatilizing, and decaying solute in variably saturated soil.

$$\left[\theta + \rho_b \frac{\partial c_p}{\partial c} + a_v \frac{\partial c_G}{\partial c} \right] \frac{\partial c}{\partial t} + \left[(1 - k_G) c \frac{\partial \theta}{\partial t} \right] + \nabla \cdot [-\theta D_{LG} \nabla c + \mathbf{u} c] = \quad (4-87)$$

$$R_L + R_P + R_G + S_c$$

Equation 4-87 is implemented in the Solute Transport application mode. The first bracketed term explains the change in solute mass per volume per time for the liquid-, solid-, and air-phase concentrations. The second term explains the changes in storage because the water content in the soil varies in time. The third bracketed expression represents the overall solute flux due to liquid dispersion, diffusion (liquid and air), and advection with moving water. The right side explains reactions and generalized sources.

Solute spreading now includes mechanical dispersion in water plus molecular diffusion for water and air. These three processes appear in the liquid-gas dispersion tensor, whose entries are

$$\theta D_{LGii} = \alpha_1 \frac{u_i^2}{|\mathbf{u}|} + \alpha_2 \frac{u_j^2}{|\mathbf{u}|} + \theta D_m \tau_L + a_v D_G k_G \tau_G \quad (4-88)$$

$$\theta D_{LGij} = \theta D_{LGji} = (\alpha_1 - \alpha_2) \frac{u_i u_j}{|\mathbf{u}|} \quad (4-89)$$

In this equation, D_{LGii} are the principal components of the liquid-gas dispersion tensor; D_{LGij} and D_{LGji} are the cross terms; α is the dispersivity (m) where the subscripts 1 and 2 denote longitudinal and transverse flow, respectively. D_m and D_G (m^2/d) are molecular diffusion, while τ_L and τ_G give the tortuosity factors for liquid (water) and gas (air), respectively.

The three solutes—aldicarb, aldicarb sulfoxide, and aldicarb sulfone—have different decay terms, R_{Li} , partition coefficients, k_{pi} , and volatilization constants, k_{Gi} . All of the solutes attach to soil particles. Two of the solutes volatilize; sulfoxide does not.

Results

First, review the results of the perfectly mixed reactor model, solved in the Reaction Engineering Lab.

Figure 4-41 shows the concentration profile of aldicarb and all of its decay products. Only small amounts of aldicarb remain after 10 days. Figure 4-42 shows concentration transients of the most toxic species aldicarb, aldicarb sulfoxide, and aldicarb sulfone, as well as the sum of these three components (see Figure 4-39 for LD_{50} values).

Considering the summed contributions, contamination levels clearly remain high even after several months.

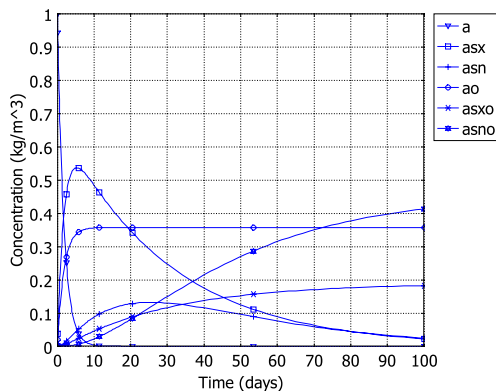


Figure 4-41: Concentration profiles (kg/m^3) as reactions occur during a 100 day time period.

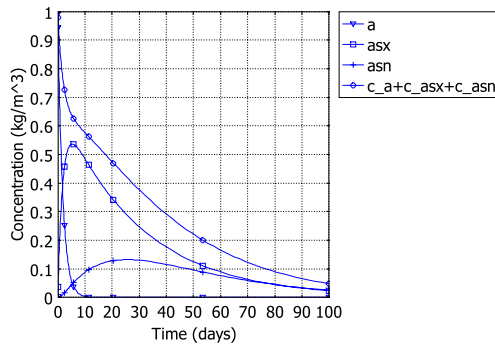


Figure 4-42: Concentration transients of the most toxic species, aldicarb (c_a), aldicarb sulfoxide (c_{asx}), and aldicarb sulfone (c_{asn}).

Results shown below come from the space and time-dependent model set up and solved in COMSOL Multiphysics.

Figure 4-43 shows the fluid flow in soil after 0.3 days (left) and 1.0 days (right). The plots illustrate the wetting of the soil with time. As indicated by the arrows, the fluid velocities are relatively high beneath the ponded water.

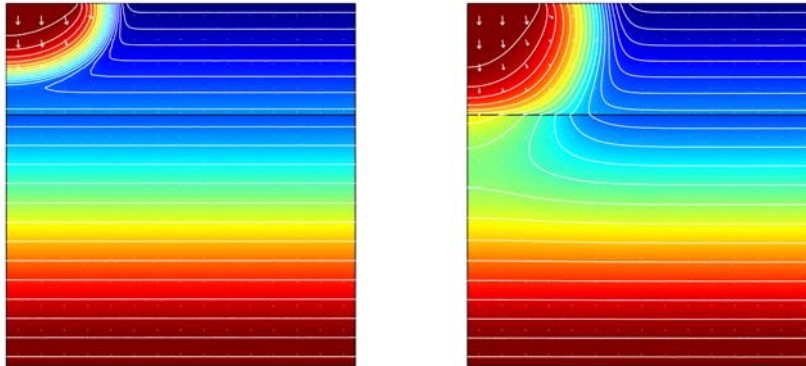


Figure 4-43: The effective saturation (surface plot), pressure head (contours), and flow velocity (arrows) in a variably saturated soil after 0.3 days (left) and 1 day (right).

Figure 4-44 through Figure 4-46 show the concentration distribution of aldicarb and the equally toxic aldicarb sulfoxide, after 1, 5, and 10 days of infiltration. Consistent with the evolving flow field, the main direction of transport is in the vertical direction.

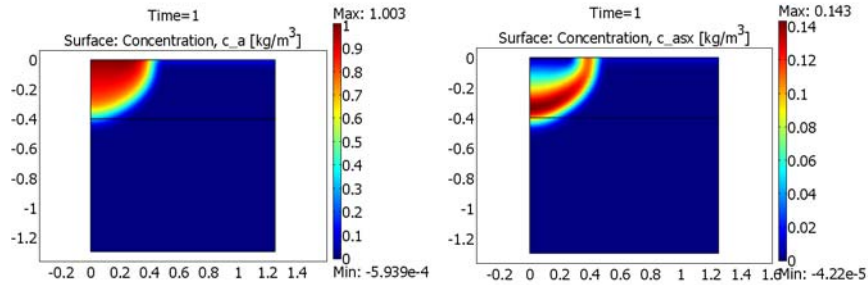


Figure 4-44: Concentration of aldicarb (left) and aldicarb sulfoxide (right) after 1 day.

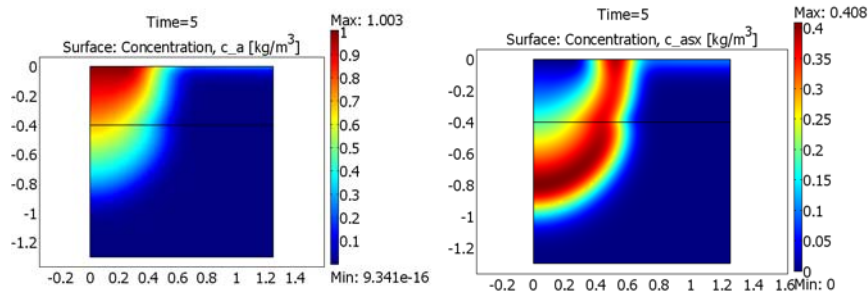


Figure 4-45: Concentration of aldicarb (left) and aldicarb sulfoxide (right) after 5 days.

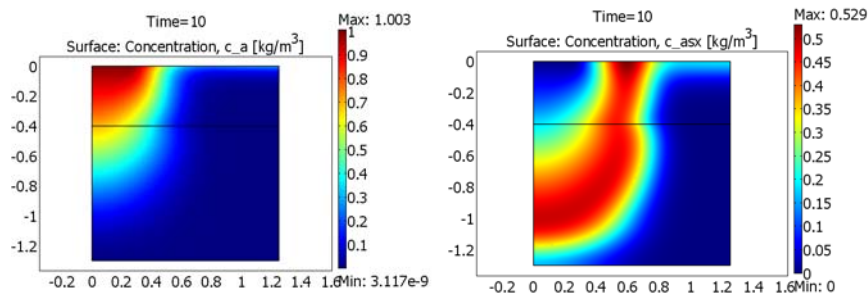


Figure 4-46: Concentration of aldicarb (left) and aldicarb sulfoxide (right) after 10 days.

The distribution of aldicarb has clearly reached steady-state conditions after 10 days. This time frame was also predicted by the ideal reactor model. Results also show that the soil contamination is rather local with respect to the aldicarb source. The aldicarb sulfoxide, on the other hand, can be expected to affect a considerably larger soil volume for a significantly longer time.

References

1. J. Bear, J., *Hydraulics of Groundwater*, McGraw-Hill Inc., 1978.
2. M.Th. van Genuchten, "A closed-form equation for predicting the hydraulic of conductivity of unsaturated soils," *Soil Sci. Soc. Am. J.*, vol. 44, pp. 892–898, 1980.

Model Library path: Reaction_Engineering_Lab/Earth_Science/
pesticide_transport

Modeling Using the COMSOL Reaction Engineering Lab

MODEL NAVIGATOR

- 1 Start COMSOL Reaction Engineering Lab.
- 2 Click **New** in the **Model Navigator**.

OPTIONS AND SETTINGS

- 1 Click the **Model Settings** button on the Main toolbar.
- 2 Select the **Liquid** from the **Reacting fluid** list.
- 3 Select the **Calculate thermodynamic properties** check box.
- 4 Select the **Calculate species transport properties** check box.
- 5 Click **Close**.

REACTIONS INTERFACE

- 1 Click the **Reaction Settings** button on the Main toolbar.
- 2 Make sure the **Reactions** page is active. Create five entries in the **Reaction selection** list by clicking the **New** button

- 3 Enter the following reaction formulas by first selecting the appropriate row in the **Reaction selection** list and then entering the corresponding text in the **Formula** edit field.

REACTION ID #	REACTION FORMULA
1	a=>asx
2	asx=>asn
3	a=>a0
4	asx=>asx0
5	asn=>asn0

- 4 Type in the following rate constants by first selecting the appropriate row in the **Reaction selection** list and then entering the corresponding value in the **k^f** edit field.

REACTION ID #	FORWARD RATE CONSTANT
1	0.36
2	0.024
3	0.2
4	0.01
5	0.0524

SPECIES INTERFACE

- 1 Click the **Species** tab.
- 2 Select the entry **a** from the **Species selection** list and type 1 in the **c₀** edit field.
- 3 Go to the **Transport** page.
- 4 Select all entries in the **Species selection** list by pressing Ctrl+A and clicking the list.
- 5 Click the **Specify diffusivity** check box and type 0.00374 in the **Diffusivity** edit field.
- 6 Click **Close**.

COMPUTING THE SOLUTION

- 1 Click the **Solver Parameters** button on the Main toolbar.
- 2 Go to the **Times** edit field and enter 100. Note that the time unit in this example is days.
- 3 Click **OK**.
- 4 Compute the solution by clicking the **Solve** button on the Main toolbar.

POSTPROCESSING AND VISUALIZATION

The concentration transients of all species are plotted by default as shown in Figure 4-41. Reproduce Figure 4-42 with the following steps:

- 1 Click the **Plot Parameters** button on the Main toolbar.
- 2 Remove the entries ao, asxo, asno from the **Quantities to plot** list by selecting them and clicking the < button.
- 3 Type $c_a+c_{asx}+c_{asn}$ in the **Expression** edit field and click the associated > button.
- 4 Click **OK**.

Now, move on to export the reaction model to COMSOL Multiphysics and solve the time and space-dependent transport and reaction problem.

SPECIES INTERFACE

This model focuses on the concentration of the highly toxic species aldicarb (a), aldicarb sulfoxide (asx), and aldicarb sulfone (asn). Therefore, you can disregard the mass balances for the hydrogenolysis products (ao, asxo, and asno). Before exporting the reaction model you therefore deactivate these species.

- 1 Click the **Reaction Settings** button on the Main toolbar.
- 2 Click the **Species** page.
- 3 Select **ao** from the **Species selection** list and deactivate the species by clearing the check box immediately to the left of the species name.
- 4 In the same way, deactivate the species asxo and asno.
- 5 Click **Close**.

EXPORT SETTINGS

- 1 Click the **Export to COMSOL Multiphysics** button on the Main toolbar.
- 2 Select **Axial symmetry (2D)** from the **Space dimension** list, then click **OK**.
- 3 The **Export to COMSOL Multiphysics** dialog box appears.
- 4 Go to the **Export mass balance** area, and in the **Application mode** list select **Solute Transport: New**.
- 5 In the **Group name** edit field type reactions.
- 6 Move to the **Export energy balance** area and clear the check box in the upper left corner.

- 7 Go to the **Export momentum balance** area and clear the check box in the upper left corner.
- 8 Click the **Export** button at the bottom of the dialog box.

Modeling Using COMSOL Multiphysics

Click the **COMSOL Multiphysics** window.

- 1 Select the menu item **Multiphysics>Model Navigator**.
Note how the model already contains the application mode **Solute Transport**, created by the export from Reaction Engineering Lab.
- 2 In the list of application modes select **Earth Science Module>Fluid Flow>Richards' Equation>Pressure head analysis>Transient analysis**.
- 3 Click the **Add** button.
- 4 Click **OK**.

APPLICATION SCALAR VARIABLES

To set the vertical direction and gravitational constant in the model, go to the **Physics** menu and choose **Scalar Variables**. Make the following modifications to the defaults. Here you convert from seconds to days and square the quantity because you are dealing with acceleration. When done, click **OK**.

NAME	EXPRESSION
g_esvr	9.82*86400*86400
D_esvr	z

GEOMETRY MODELING

You create the geometry by drawing two rectangles and adding one line.

- 1 Select the menu item **Draw>Specify Objects>Rectangle**. Specify the following settings, then click **OK**.

PARAMETER	EXPRESSION
Width	1.25
Height	1.3
r	0
z	-1.3

- 2 Go to the Main toolbar and click the **Zoom Extents** button.

- 3 Again select **Draw>Specify Objects>Rectangle**. Specify the following settings, then click **OK**.

PARAMETER	EXPRESSION
Width	1 . 25
Height	0 . 4
r	0
z	-0 . 4

- 4 Select the menu item **Draw>Specify Objects>Line**. In the **r** edit field enter 0 0.25, and in the **z** edit field enter 0 0. Click **OK**.

PHYSICS—SOLUTE TRANSPORT

- 1 Choose **Multiphysics>Solute Transport (esst)**.
- 2 Select the menu item **Physics>Properties**.
- 3 Select **Liquid/Solid/Gas** from the **Material** drop down list, then click **OK**. You change the default settings as a three phase system is being modeled.
- 4 Select the menu item **Physics>Subdomain Settings**. In the **Subdomain selection** list simultaneously select Subdomains 1 and 2 by pressing the Ctrl key.
- 5 From the **Group** list, select **reactions**.
- 6 Go to the **Flow and Media** page, enter the following settings.

PROPERTY	VALUE
θ	theta_esvr
θ_s	thetas_esvr
u	u_esvr
v	v_esvr

This couples the solute transport to the flow calculated by the Richards' Equation (esvr) application mode.

- 7 Set the **Time change in liquid volume fraction** to **Time change in pressure head** and enter the following.

PROPERTY	VALUE
C	C_esvr
$\partial H_p / \partial t$	pt

- 8 Click the **Liquid** page. In the list of subdomains, simultaneously select **1** and **2** by pressing Ctrl. Make the changes in the following table, and note that you can copy and paste in the edit fields.

TERM	C_A	C_ASX	C_ASN
α_1	0.005	0.005	0.005
α_2	0.0001	0.0001	0.0001

Note also that the **D_{mL}** and **R_L** edit fields have been filled out automatically as a result of the export from COMSOL Reaction Engineering Lab.

- 9 Click the **Solid** page. Select both Subdomain 1 and 2, then make the following changes:

TERM	C_A	C_ASX	C_ASN
ρ_b	1300	1300	1300
K_p	0.0001	0.00005	0.0002

- 10 Click the **Gas** page, select Subdomains 1 and 2, then make the following changes:

TERM	C_A	C_ASX	C_ASN
k_G	1.33e-7	0	1.33e-3
D_{mG}	0.432	0.432	0.432

- 11 Go to the **Init** page and type 0 in the **c_a(t₀)** edit field.

- 12 Click **OK**.

Boundary Conditions—Solute Transport

- 1 From the **Physics** menu choose **Boundary Settings**.
- 2 Verify that you are on the **c_a** page, then enter the following settings:

BOUNDARY	CONDITION	VARIABLE	VALUE
1, 3	Axial symmetry		
2, 7, 8	Advective flux		
5	Flux	N_0	$1e6 * (1 - c_a) * (t \geq 0)$
6	No flow boundary volatilization	d	0.005

3 Click the **c_asx** page, then enter the following settings:

BOUNDARY	CONDITION	VARIABLE	VALUE
1, 3,	Axial symmetry		
6	No flux/Symmetry		
2, 7, 8	Advective flux		
5	Concentration	c_asx ₀	0

4 Click the **c_asn** page, then enter the following settings:

BOUNDARY	CONDITION	VARIABLE	VALUE
1, 3	Axial symmetry		
2, 7, 8	Advective flux		
5	Concentration	c_asn ₀	0
6	No flow boundary volatilization	d	0.005

5 Click **OK**.

PHYSICS—RICHARDS' EQUATION

Subdomain Settings—Richards' Equation

- 1 Go to the **Multiphysics** menu and choose **Richards' Equation (esvr)**.
- 2 Select the menu item **Physics>Subdomain Settings** and click the **Coefficients** page.
Enter the following settings, then click **Apply**.

SETTINGS	SUBDOMAIN 1	SUBDOMAIN 2
Constitutive relation	van Genuchten	van Genuchten
θ_s	0.339	0.399
θ_r	0	0.0001
Storage term	User defined	User defined
S	0.339	0.399
K_S	0.454	0.298
ρ_f	1000	1000

3 Click the **van Genuchten** page and make the following changes:

SETTINGS	SUBDOMAIN 1	SUBDOMAIN 2
α	1.39	1.74

SETTINGS	SUBDOMAIN 1	SUBDOMAIN 2
n	1.6	1.38
l	0.5	0.5

- 4 Click the **Init** page. Select both subdomains simultaneously using the Ctrl key, then in the edit field enter this expression:

SETTING	SUBDOMAINS 1 AND 2
$H_p(t_0)$	$-(z+1.2)*(z<-0.4)+(-(z+1.2)-0.2*(z+0.4))*(-0.4\leq z)$

- 5 Click **OK**.

Boundary Conditions—Richards' Equation

- 1 From the **Physics** menu choose **Boundary Settings** and make these settings:

BOUNDARY	BOUNDARY CONDITION	VARIABLE	EXPRESSION
1, 3	Axial symmetry		
6–8	Zero flux/Symmetry		
2	Inward flux	N_0	$-0.454/100$
5	Mixed	R_b	$1*(t\geq 0)$
5		H_{pb}	$0.01*(t\geq 0)$
5		D_b	$D_{esvr}*(t\geq 0)$

- 2 Click **OK**.

MESH GENERATION

- 1 Go to the menu item **Mesh>Free Mesh Parameters**.
- 2 Click the **Boundary** page. Select the upper surface and the break between the two soil layers (Boundaries 4, 5, and 6). In the **Maximum element size** edit field enter 0.02.
- 3 Click **OK**.
- 4 Click the **Initialize Mesh** button on the Main toolbar.

COMPUTING THE SOLUTION

This model has many degrees of freedom and is also nonlinear. It requires roughly an hour to solve on a fast computer.

- 1 Choose **Solve>Solver Parameters**.
- 2 In the **Solver** list choose **Time dependent** if it is not already selected.

- 3 In the **Times** edit field enter `-0.1,0,logspace(-3,-1,21),0.1:0.1:1,2:1:10`.
It gives you 31 logarithmically spaced inputs from 0.001 to 0.1 day; 0.1-day increments through Day 1; and 1-day increments until Day 10.
- 4 Click the **Advanced** page.
- 5 Change the **Type of scaling** to **Manual**.
- 6 Type `p 1e10 c_a 1 c_asx 1 c_asn 1` in the **Manual scaling** edit field.
- 7 Click **OK**.
- 8 Click the **Solve** button on the Main toolbar.

POSTPROCESSING AND VISUALIZATION

To plot the flow solution in Figure 4-43, follow these steps.

- 1 Select the menu item **Postprocessing>Plot Parameters**.
- 2 On the **General** page go to the **Plot type** area and select the **Surface**, **Contour**, and **Arrow** check boxes.
- 3 From the **Solution at time** list choose **0.3**.
- 4 Click the **Surface** page, and in the **Expression** edit field enter `Se_esvr`.
- 5 Click the **Contour** page, and in the **Predefined quantities** list choose **Richards' Equation (esvr)>Pressure head**.
- 6 In the **Contour color** area, click the **Uniform color** option button. Click the **Color** button, change the color to white, and click **OK**.
- 7 Click **Apply**.
- 8 Click the **Arrow** page.
- 9 From the list of **Predefined quantities** select **Richards' Equation (esvr)>Velocity field**.
- 10 Click the **Color** button, choose white as the desired color, then click **OK**.
- 11 Clear the **Auto** check box, and in the **Scale factor** edit field enter `0.5`.
- 12 Click **Apply**.
- 13 To generate the solution after 1 day, go to the **General** page and select **1** from the **Solution at time** list, and then click **OK**.

To generate the plots in Figure 4-44 through Figure 4-46, continue with these steps:

- 1 Select the menu item **Postprocessing>Plot Parameters**.
- 2 On the **General** page, clear the **Arrow** and **Contour** check boxes.
- 3 Click the **Surface** page, then type `c_a` in the **Expression** edit field.

- 4 Click **Apply**.
- 5 To generate the solution after 5 days and 10 days, go to the **General** page and select the corresponding entries from the **Solution at time** list, and click **Apply**.
- 6 To generate plots for the aldicarb sulfoxide concentrations, click the **Surface** page, type `c_asx` in the **Expression** edit field, then click **Apply**.

Oscillating Reactions

Most reactions proceed smoothly, at varying rates, to a final state of equilibrium. Some, however, do not. They oscillate with reactant, product, or intermediate species concentrations fluctuating wildly. Such instances of nonlinear chemical dynamics are commonplace in biochemical systems.

This example looks closely at three well-known examples of reaction systems with oscillating kinetics: the Lotka reaction, the Lotka-Volterra reaction, and a version of the Belousov-Zhabotinsky reaction. To model them, you first enter the chemical reaction formulas for the mechanisms into the Reaction Engineering Lab and have it set up and solve the corresponding material balances. Then you can easily modify the reaction conditions and focus on how these choices affect the results. After these initial studies, you export the reaction models to COMSOL Script to perform additional calculations and postprocessing.

Introduction

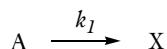
Autocatalysis is the acceleration of a reaction by the products. A consequence of autocatalysis is the possibility that the reacting species will vary periodically. Such reaction systems are of great interest, and many natural phenomena—from firefly flashes to the human heartbeat—are oscillatory chemical systems. Although the actual reaction mechanisms responsible for oscillations in biochemistry often are exceedingly complicated, surprisingly simple reaction models have successfully captured key features of these cyclic events.

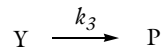
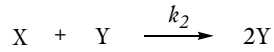
The following discussion investigates three oscillating reaction models (Ref. 1 and Ref. 2).

Model Descriptions

CASE 1—THE LOTKA REACTION

Lotka originally created this simple example chemistry to illustrate a temporal behavior characterized by damped oscillations. Lotka's mechanism is given by the following set of reaction steps:





The second reaction is autocatalytic, that is, the first reaction produces X, which is consumed in the following step. In these reactions, the species P symbolizes reaction products that do not affect the oscillations.

The mass action law suggests the following reaction rates ($\text{mol}/(\text{m}^3 \cdot \text{s})$) for the previously described system:

$$r_1 = k_1 c_A$$

$$r_2 = k_2 c_X c_Y$$

$$r_3 = k_3 c_Y$$

Making use of the reaction rates and the stoichiometry of the reaction formulas, the material balances for the species become

$$\frac{dc_A}{dt} = -r_1$$

$$\frac{dc_X}{dt} = r_1 - r_2$$

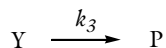
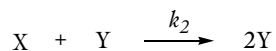
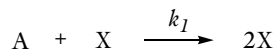
$$\frac{dc_Y}{dt} = r_2 - r_3$$

$$\frac{dc_P}{dt} = r_3$$

The Reaction Engineering Lab automatically generates these reaction rate expressions and material balances. You simply enter the chemical reaction formulas into the user interface.

CASE 2—THE LOTKA-VOLTERRA REACTION

Volterra proposed a mechanism for interacting organisms related to the Lotka mechanism. The Lotka-Volterra kinetic scheme differs from the Lotka scheme only by the fact that the first reaction step is also autocatalytic:



This mechanism is also known as the prey-predator scheme, displaying steady species that oscillate without damping.

The mass action law suggests the following reaction rates ($\text{mol}/(\text{m}^3 \cdot \text{s})$) for the system just described:

$$r_1 = k_1 c_A c_X$$

$$r_2 = k_2 c_X c_Y$$

$$r_3 = k_3 c_Y$$

The material balance equations for a perfectly mixed isothermal system become

$$\frac{dc_A}{dt} = -r_1$$

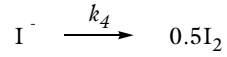
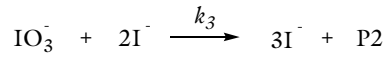
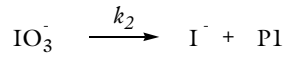
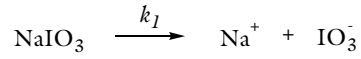
$$\frac{dc_X}{dt} = r_1 - r_2$$

$$\frac{dc_Y}{dt} = r_2 - r_3$$

$$\frac{dc_P}{dt} = r_3$$

CASE 3—THE BELOUSOV-ZHABOTINSKY REACTION

Originally, Belousov wanted to reproduce the chemistry of the citric acid cycle—work later carried on by Zhabotinsky. The full mechanism of the Belousov-Zhabotinsky reaction involves more than 40 reaction steps. However, a smaller mechanism consisting of four reactions captures the reaction's oscillating behavior. Consider this example:



In these reactions, the species P1 and P2 symbolize reaction products that do not affect the oscillations. The reaction rates for the system become

$$r_1 = k_1 c_{\text{NaIO}_3}$$

$$r_2 = k_2 c_{\text{IO}_3^-}$$

$$r_3 = k_3 c_{\text{IO}_3^-} c_{\text{I}^-}^2$$

$$r_4 = k_4 c_{\text{I}^-}$$

Not considering the product species P1 and P2, the material balance equations become

$$\frac{dc_{\text{NaIO}_3}}{dt} = -r_1$$

$$\frac{dc_{\text{Na}}}{dt} = r_1$$

$$\frac{dc_{\text{IO}_3^-}}{dt} = r_1 - r_2 - r_3$$

$$\frac{dc_{\text{I}^-}}{dt} = r_2 + r_3 - r_4$$

$$\frac{dc_{\text{I}_2}}{dt} = 0.5r_4$$

Note again that all of these equations are automatically defined in the Reaction Engineering Lab.

Results

Compare the time evolution of the three reacting systems by solving the material balances and plotting the species concentrations as functions of time. To increase the understanding of the dynamic chemistries, also create plots for the trajectories of the oscillating species, ($c_X(t)$, $c_Y(t)$).

CASE I—THE LOTKA REACTION

As shown in Figure 4-47, the Lotka scheme corresponds to damped oscillating reactions, in this case reaching equilibrium after approximately 4000 s.

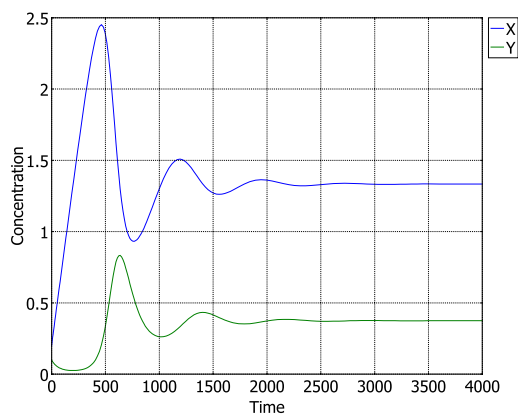


Figure 4-47: Species concentrations (mol/m^3) as functions of time (s). The system reaches equilibrium after approximately 4000 s.

Figure 4-48 shows two phase plots—that is, trajectories in the (c_X, c_Y) plane, here parameterized by the time, t . The two trajectories start at the initial points $(c_X, c_Y) = (0.2, 0.1)$ and $(c_X, c_Y) = (0.5, 0.8)$, respectively.

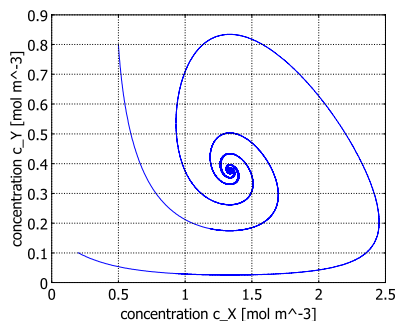


Figure 4-48: Trajectories $\{(c_X(t), c_Y(t))\}$ given in molar concentrations (mol/m^3). The system reaches the same stationary state irrespective of the starting conditions.

It is clear from the graphs that the same stationary state is reached irrespective of initial concentrations.

CASE2—THE LOTKA-VOLTERRA REACTION

The Lotka-Volterra kinetics illustrates chemical oscillations without damping (Figure 4-49).

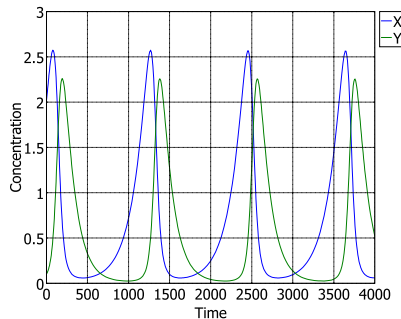


Figure 4-49: Species concentrations (mol/m^3) of oscillating species as functions of time (s).

Figure 4-50 provides phase plots, $\{(c_X(t), c_Y(t))\}$, of the system. The two trajectories start at the points $(c_X, c_Y) = (2, 0.1)$ and $(c_X, c_Y) = (1.5, 1)$, respectively.

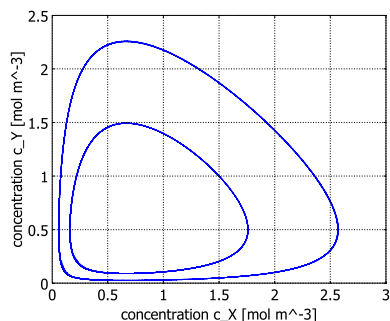


Figure 4-50: Trajectories $\{(c_X(t), c_Y(t))\}$ given in molar concentrations (mol/m^3). The closed orbits illustrate the undamped nature of the system.

The plots indicate that every set of initial conditions produces a different orbit. In biological systems, however, it is common that a number of initial conditions lead to the same oscillatory pattern. These stable patterns are referred to as attractor orbits.

CASE 3—THE BELOUSOV-ZHABOTINSKY REACTION

From Figure 4-51 it appears as if the Belousov-Zhabotinsky reaction has the same oscillatory behavior as the Lotka-Volterra reaction.

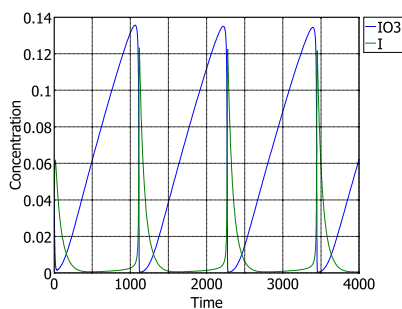


Figure 4-51: Species concentrations (mol/m^3) as functions of time (s).

However, the phase plots in Figure 4-52 illustrate a fundamental difference between the two situations.

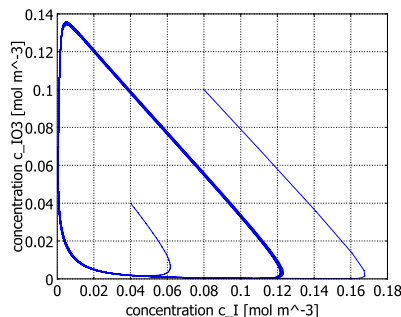


Figure 4-52: Trajectories $\{c_I(t), c_{IO_3}(t)\}$ given in molar concentrations (mol/m^3). Initial concentrations are $(c_I, c_{IO_3}) = (0.04, 0.04)$ and $(c_I, c_{IO_3}) = (0.01, 0.08)$ (mol/m^3). The system reaches the same limit cycle irrespective of the starting conditions.

Irrespective of the initial concentrations of the species I and IO_3 , the Belousov-Zhabotinsky mechanism settles into the same periodic variations of concentration. As mentioned previously, this is a common feature observed in oscillating biological systems, and indeed the Belousov-Zhabotinsky mechanism has been used extensively to model nonlinear dynamics in biology.

To conclude, the Reaction Engineering Lab here examines oscillating reactions. The software's ease of use enables you to focus on modeling results rather than the model setup and methods of solution. This example studies three reaction mechanisms with different sets of initial conditions, and it provides several important insights into the field of nonlinear chemical dynamics.

References

1. M.M.C. Ferreira, W.C. Ferreira Jr., A.C.S. Lino, and M.E.G. Porto, *J. Chem. Education*, vol. 76, p. 861, 1999.
2. H.S. Fogler and M.N. Gurmen,
http://www.engin.umich.edu/~cre/web_mod/oscil/module.htm.

Model Library path: Education/oscillating_reactions_lotka

Model Library path: Education/oscillating_reactions_lv

Model Library path: Education/oscillating_reactions_bz

Modeling Using COMSOL Reaction Engineering Lab

MODEL NAVIGATOR

- 1 Start the Reaction Engineering Lab.
- 2 Click **New** in the **Model Navigator**.

REACTIONS INTERFACE—CASE 1

- 1 Choose **Model>Reaction Settings**.
- 2 Create three entries in the **Reaction selection** list by clicking the **New** button three times.
- 3 Enter the following reaction formulas by first selecting the appropriate row in the **Reaction selection** list and then typing the text in the **Formula** edit field. Note how the reaction rate expressions are automatically generated and presented in the **r** edit field.

REACTION ID #	REACTION FORMULA
1	$A \Rightarrow X$
2	$X + Y \Rightarrow 2Y$
3	$Y \Rightarrow P$

- 4 Enter the following forward rate constants by first selecting the appropriate row in the **Reaction selection** list and then typing the numbers in the **k^f** edit field:

REACTION ID #	k ^f
1	6e-3
2	1.2e-2
3	1.6e-2

SPECIES INTERFACE—CASE I

- 1 Click the **Species** tab.
- 2 Verify that the **Species selection** list contains the four species A, X, Y, and P.
- 3 On the **General** page, enter the following initial concentrations, one by one, in the **c₀** edit field after first having selected the appropriate entry in the **Species selection** list:

SPECIES NAME	c ₀
A	1
X	0.2
Y	0.1
P	0

- 4 Select the reactant species A in the **Species selection** list and select the **Lock concentration/activity** check box. This removes the material balance for species A. The concentration of this species is assumed to have the constant value entered in the **c₀** edit field.
- 5 Click **Close**.

COMPUTING THE SOLUTION—CASE I

- 1 Choose **Simulation>Solver Parameters**.
- 2 In the **Times** edit field, type 0 4000.
- 3 In the **Relative tolerance** edit field, type 1e-4.
- 4 In the **Absolute tolerance** edit field, type 1e-5.
- 5 Clear the **Stop if steady state is reached first** check box.
- 6 Click **OK**.
- 7 Click the **Solve Problem** button (=) on the Main toolbar.

POSTPROCESSING AND VISUALIZATION—CASE I

The default plot shows all concentrations versus time. To create Figure 4-47, proceed with the following steps:

- 1 Choose **Postprocessing>Plot Parameters**.
- 2 From the **Quantities to plot** list, select the entries **A** and **P**.
- 3 Remove the entries from the list by clicking the **<** button.
- 4 Click **OK**.

- 5 Choose **File>Save As** and save the reaction model as `oscillating_reactions_lotka.rxn`.

Next, modify the first model.

REACTIONS INTERFACE—CASE 2

- 1 Choose **Model>Reaction Settings**.
- 2 Click the **Reactions** tab and select the first reaction.
- 3 Edit the reaction to read $A+X \Rightarrow 2X$ by typing this expression in the **Formula** edit field.
- 4 Select the last reaction in the **Reaction selection** list and type $8e-3$ in the k^f edit field.

SPECIES INTERFACE—CASE 2

- 1 Click the **Species** tab.
- 2 Select species **X** in the **Species selection** list and type 2 in the c_0 edit field.
- 3 Click **Close**.

COMPUTING THE SOLUTION—CASE 2

Click the **Solve Problem** button on the Main toolbar to solve the problem with the new settings.

POSTPROCESSING AND VISUALIZATION—CASE 2

- 1 The initial plot will now resemble Figure 4-49.
- 2 Choose **File>Save as** and save the reaction model as `oscillating_reactions_lv.rxn`.

REACTIONS INTERFACE—CASE 3

- 1 Select **File>New** to create a new reaction model.
- 2 Choose **Model>Reaction Settings**.
- 3 Create four entries in the **Reaction selection** list by clicking the **New** button four times.
- 4 Enter the following reaction formulas by first selecting the appropriate row in the **Reaction selection** list and then typing the text in the **Formula** edit field:

REACTION ID #	REACTION FORMULA
1	$\text{NaIO}_3 \Rightarrow \text{Na} + \text{IO}_3$
2	$\text{IO}_3 \Rightarrow \text{I} + \text{P1}$

REACTION ID #	REACTION FORMULA
3	$\text{IO}_3 + 2\text{I} \Rightarrow 3\text{I} + \text{P}_2$
4	$\text{I} \Rightarrow 0.5\text{I}_2$

- 5 Enter the following forward rate constants by first selecting the appropriate row in the **Reaction selection** list and then typing the numbers in the **k^f** edit field:

REACTION ID #	k ^f
1	1.67e-5
2	1.67e-4
3	41.7
4	1.67e-2

SPECIES INTERFACE—CASE 3

- 1 Click the **Species** tab.
- 2 Verify that the **Species selection** list contains the seven species expected from entering the reaction formulas above.
- 3 On the **General** page, enter the following initial concentrations, one by one, in the **c₀** edit field after first having selecting the appropriate entry in the **Species selection** list:

SPECIES NAME	c ₀
NaIO ₃	10
Na	0
IO ₃	4e-2
I	4e-2
PI	0
P ₂	0
I ₂	0

- 4 Click **Close**.

COMPUTING THE SOLUTION—CASE 3

- 1 Choose **Simulation>Solver Parameters**.
- 2 In the **Times** edit field, type 0 4000.
- 3 In the **Relative tolerance** edit field, type 1e-7.
- 4 In the **Absolute tolerance** edit field, type 1e-8.

- 5 Clear the **Stop if steady state is reached first** check box.
- 6 Click **OK**.
- 7 Click the **Solve Problem** button on the Main toolbar to solve the model.

POSTPROCESSING AND VISUALIZATION—CASE 3

To create Figure 4-51, follow these steps:

- 1 Choose **Postprocessing>Plot Parameters**.
- 2 Click the **<<** button to clear the default selection in the **Quantities to plot** list.
- 3 From the **Predefined quantities** list, select the entries **I** and **I03**.
- 4 Click the **>** button to add the selection to the **Quantities to plot** list.
- 5 Click **OK**.
- 6 Choose **File>Save As** and save the reaction model as `oscillating_reactions_bz.rxn`.

Modeling Using COMSOL Script

Now solve the reaction models for different sets of initial concentrations and then plot the solutions obtained in the phase plane, (c_X, c_Y) . This is straightforward to implement in COMSOL Script.

EXPORT—CASE 1

- 1 In the Reaction Engineering Lab, load the Lotka reaction model by choosing **File>Open** and typing `oscillating_reactions_lotka.rxn` in the **File name** edit field.
- 2 Choose **File>Export>REL Structure to Workspace as 'rel'**. COMSOL Script will launch, if not already open.

SCRIPTING—CASE 1

- 1 Click the **COMSOL Script** window.

You can choose between using the ready-made script that comes with the model or typing it in yourself. If you choose to run the ready-made script, you can skip the next step where the script is created and saved and continue with Step 7.

- 2 If you choose to type it in yourself, type `edit` at the prompt to bring up a **COMSOL Script Editor** window.
- 3 Type the following script into the **COMSOL Script Editor**:

```

% Create vectors containing initial concentrations
cX = [0.2 0.5];
cY = [0.1 0.8];

%create a loop
for i = 1:2
% solve the reaction model
rel.sol=femtime(rel, 'report','off', ...
'solcomp',{'c_X','c_Y','c_P'}, ...
'outcomp',{'c_X','c_Y','c_P'}, ...
'const',{'c0_X',cX(i),'c0_Y',cY(i)}, ...
'atol',1e-4, ...
'rtol',1e-5, ...
'tlist',0:1:4000);

%Plot the results for each simulation
postglobalplot(rel,'c_Y','linxdata','c_X', ...
'axislabel',{'concentration c_X [mol m^-3]','concentration c_Y
[mol m^-3]'});
hold on

%end loop
end

hold off

```

- 4 Choose **File>Save** to save the file and specify the name as `oscillating_reactions_lotka.m`.
- 5 Return to the **COMSOL Script** window.
- 6 Run the script by choosing **File>Run M-file**. Browse to where you saved the file, select it, and click **Open** to generate Figure 4-48.
- 7 To run the ready-made script, simply choose **File>Run M-file** and browse to `models/Reaction_Engineering_Lab/Education/oscillating_reactions_lotka.m` in the COMSOL installation directory.
- 8 Click **OK** to generate Figure 4-48.

EXPORT—CASE 2

- 1 In the Reaction Engineering Lab, load the Lotka-Volterra reaction model by selecting **File>Open** and browse to `oscillating_reactions_lv.rxn`.
- 2 Choose **File>Export>REL Structure to Workspace as 'rel'**.

SCRIPTING—CASE 2

- 1 Click the **COMSOL Script** window.

If, in Case 1 above, you chose to run the ready-made script, skip the first few steps below and start directly with Step 7; otherwise, follow Steps 2–6.

- 2 Type `edit oscillating_reactions_lotka.m` to open the text editor.
- 3 In the **Script Editor**, choose **File>Save as** and save the file as `oscillating_reactions_lv.m`.
- 4 Modify the initial concentration vectors as follows:

```
cX = [2 1.5];  
cY = [0.1 1];
```
- 5 Choose **File>Save**.
- 6 Run the script by choosing **File>Run M-file**. Browse to where you saved the file, select it, and click **Open** to generate Figure 4-50.
- 7 To run the ready-made script, choose **File>Run M-file** and browse to `models/Reaction_Engineering_Lab/Education/oscillating_reactions_lv.m` in the COMSOL installation directory.
- 8 Click **OK** to generate Figure 4-50.

EXPORT—CASE 3

- 1 In the Reaction Engineering Lab, load the Belousov-Zhabotinsky reaction model by choosing **File>Open** and specifying the file name `oscillating_reactions_bz.rxn`.
- 2 Choose **File>Export>REL Structure to Workspace as 'rel'**.

SCRIPTING—CASE 3

- 1 Click the **COMSOL Script** window.

Again, you can choose between using the ready-made script that comes with the model or typing it in yourself. If you choose to run the ready-made script, you can skip the next few steps where the script is created and saved, and continue with Step 7.

- 2 If you choose to type it in yourself, type `edit` at the prompt to bring up a **COMSOL Script Editor** window.
- 3 Type the following script into the **COMSOL Script Editor**:

```
close all;  
% Create vectors containing initial concentrations  
cI = [0.04 0.08];  
cI03 = [0.04 0.1];
```

```

%create a loop
for i = 1:2
% solve the reaction model
rel.sol=femtime(rel, 'report','off', ...
'solcomp',{'c_NaIO3','c_Na','c_IO3','c_I','c_I2'}, ...
'outcomp',{'c_NaIO3','c_Na','c_IO3','c_I','c_I2'}, ...
'const',{'c0_I',cI(i),'c0_IO3',cIO3(i)}, ...
'atol',1e-7, ...
'rtol',1e-8, ...
'tlist',0:1:4000);

%Create the phase plots for each simulation
postglobalplot(rel,'c_IO3','linxdata','c_I', ...
'axislabel',{'concentration c_I [mol m^-3]','concentration c_IO3
[mol m^-3]}');
hold on

%end loop
end

hold off

```

- 4 Choose **File>Save** to save the file and specify the name as `oscillating_reactions_bz.m`.
- 5 Return to the **COMSOL Script** command window.
- 6 Run the script by choosing **File>Run M-file**. Browse to where you saved the file, select it, and click **Open** to generate Figure 4-52.
- 7 To run the ready-made script, simply choose **File>Run M-file** and browse to `models/Reaction_Engineering_Lab/Education/oscillating_reactions_bz.m` in the COMSOL installation directory.
- 8 Click **OK** to generate Figure 4-52.

Analyzing Pressure-Time Data in Parameter Estimation

Introduction

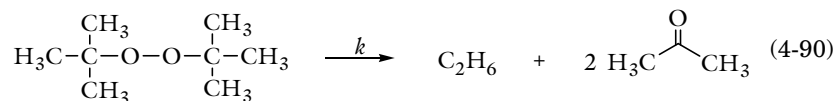
This example illustrates the estimation of the reaction order and rate constant for the gas phase decomposition of di-tert-butyl peroxide. The reaction takes place in a closed vessel of constant volume where the total pressure is measured as a function of reaction time.

The parameter estimation functionality of the Reaction Engineering Lab is directly integrated into the software's graphical user interface. As such, it allows for seamless calibration and validation of your model with respect to experimental results, before advancing to reactor analysis and design. Once experimental data has been imported, you can make use of predefined reactor types and automatically generated kinetics to evaluate the kinetic parameters of the model.

Model Definition

This example reproduces results found in Ref. 1.

Gas phase di-tert-butyl peroxide decomposes into ethane and dimethyl ketone in a batch reactor of fixed volume.



The reactor contains pure peroxide initially and is held at a constant temperature of 170 °C. In order to evaluate the reaction order as well as the rate constant, experiments are performed where the total pressure (Pa) in the reactor is measured as a function of time (s).

TIME	PRESSURE
60	1.15E+03
120	1.31E+03
180	1.43E+03
240	1.56E+03

TIME	PRESSURE
300	1.66E+03
360	1.75E+03
420	1.86E+03
480	1.95E+03
540	2.04E+03
600	2.09E+03
660	2.17E+03
720	2.23E+03
780	2.29E+03
840	2.36E+03
900	2.40E+03
960	2.43E+03
1020	2.49E+03
1080	2.53E+03
1140	2.56E+03
1200	2.60E+03

MASS BALANCES

The mass balances describing a perfectly mixed reactor with constant volume are summarized by

$$\frac{dc_i}{dt} = R_i \quad (4-91)$$

where c_i represents the species concentration (mol/m³), and R_i denotes the species rate expression (mol/(m³·s)). The reaction rate is given by:

$$r = kc_{\text{DTP}}^\alpha \quad (4-92)$$

where, α indicates the reaction order. Taking the reaction stoichiometry into account the species mass balances are:

$$\frac{dc_{\text{DTP}}}{dt} = -r \quad (4-93)$$

$$\frac{dc_{Et}}{dt} = r \quad (4-94)$$

$$\frac{dc_{\text{DMK}}}{dt} = 2r \quad (4-95)$$

Solving the mass balances provides the evolution of the species concentrations with time. Correlating the simulated results with the experimental data requires a relation between the total concentration and the total pressure. This relation is given by the ideal gas law:

$$p = \sum c_i R_g T \quad (4-96)$$

where R_g is the ideal gas constant (J/(mol·K)), and T the temperature (K).

The total pressure is calculated automatically in the Reaction Engineering Lab, and you find the expression in the **Model Settings** dialog box.

Results

The plots below show the simulation results along with the experimental data points. In each instance, the reaction order has been held constant ($\alpha = 0, 1$, and 2) while the rate constant has been estimated.

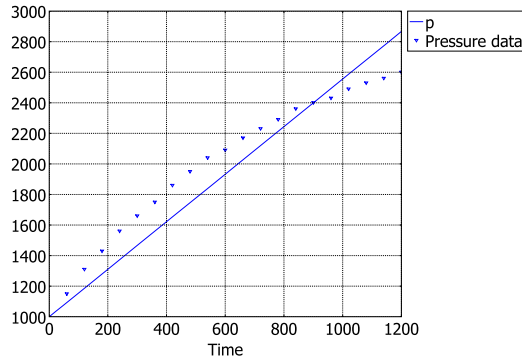


Figure 4-53: Simulated results and experimental data showing the total pressure in the reactor as a function of time. The reaction order α is 0.

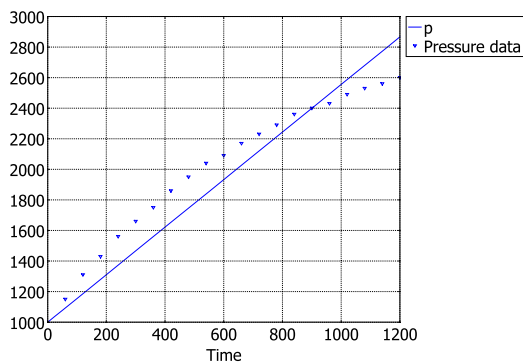


Figure 4-54: Simulated results and experimental data showing the total pressure in the reactor as a function of time. The reaction order α is 1.

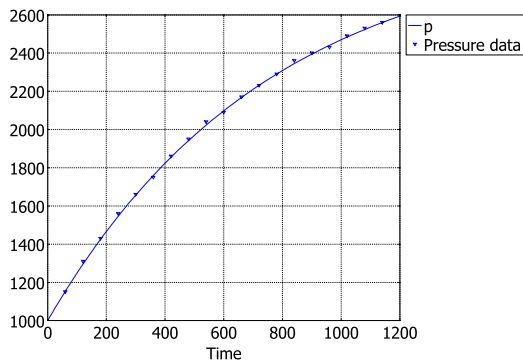


Figure 4-55: Simulated results and experimental data showing the total pressure in the reactor as a function of time. The reaction order α is 2.

Clearly, a first order reaction gives the best fit to data. If $\alpha = 1$ the corresponding rate constant is estimated to be $1.33 \cdot 10^{-3} \text{ (1/s)}$.

References

1. H. S. Fogler, *Elements of Chemical Reaction Engineering 3rd Ed.* Prentice Hall PTR, 1999, pp. 229–239.

Model Library path: Education/pressure_time

Modeling Using the COMSOL Reaction Engineering Lab

MODEL NAVIGATOR

- 1 Start the **COMSOL Reaction Engineering Lab**.
- 2 In the **Model Navigator** click the **New** button.

OPTIONS AND SETTINGS

Start by setting up constants and expressions used in the model.

- 1 Select the menu item **Model>Constants** and type in the following entries:

NAME	EXPRESSION	DESCRIPTION
alfa	0	reaction order
p0	1000	initial pressure

- 2 Click **OK**.
- 3 Select **Model>Expressions** and type in the following entries:

NAME	EXPRESSION	DESCRIPTION
c0	$p0/Rg/T$	DTP initial concentration (mol/m ³)

- 4 Click **OK**.
Continue with global model settings.
- 5 Click the **Model Settings** button on the Main toolbar.
- 6 On the **General** page type 273.15+170 in the **Temperature** edit field.
- 7 Click **Close**.

REACTIONS INTERFACE

- 1 Click the **Reaction Settings** button on the Main toolbar.
- 2 Create a new entry in the **Reaction selection** list by clicking the **New** button.
- 3 Type DTP=>ET+2DMK in the **Formula** edit field.
- 4 Edit the predefined reaction rate expression to include the reaction order. Type $kf_1 \cdot c_DTP^{alfa}$ in the **r** edit field.

SPECIES INTERFACE

- 1 Click the **Species** page.
- 2 Select **DTP** in the **Species selection** list, then type c_0 in the **c_0** edit field.
- 3 Click **Close**.

PARAMETER ESTIMATION

- 1 Click the **Parameter Estimation Settings** button on the Main toolbar.
- 2 In the **Data set selection** area, click the **Import From File** button.
- 3 Browse to the file `pressure_time_data.txt`, select it and click **Import**.
- 4 Select the **pressure_time_data.txt** entry in the **Data set selection** list.
- 5 Go to the **Variable Mapping** page and select the **Pressure data** entry in the **Data selection** list.
- 6 Type $Rg \cdot T \cdot (c_{DTP} + c_{ET} + c_{DMK})$ in the **Expression** edit field.

This associates the measured pressure with an expression for the pressure defined in the model. Equivalently you could type p in the **Expression** edit field, as Reaction Engineering Lab automatically calculates the pressure according to Equation 4-96. You find this relation defined in the **Model Settings** dialog box, in the **Pressure** edit field.

- 7 Click the **Parameters** page.
- 8 Select **kf_1 (Forward rate constant 1)** from the list of **Predefined parameters**, then click the **>** button.
- 9 Click **OK**.

COMPUTING THE SOLUTION

Click the **Estimate Parameters** button on the Main toolbar to find kf_1 for $\alpha = 0$.

Note that the software automatically updates the reaction model with the new parameter value. In this example, you find the updated value in the **Forward rate constant** edit field, in the **Reaction Settings** dialog box. Also, the software automatically runs the model simulation with the updated parameters. You can change these settings on the **Advanced** page in the **Parameter Estimation Settings** dialog box.

POSTPROCESSING AND VISUALIZATION

By default, the model plots the concentration transients of species with a nonzero initial concentration. Reproduce Figure 4-53 with the following steps:

- 1 Click the **Plot Parameters** button on the Main toolbar.

- 2 Remove all entries from the **Quantities to plot** list by clicking the << button.
- 3 In the **Expression** edit field type p , then click the > button.
- 4 Click **OK**.
- 5 Select the menu item **Model>Constants** and set the reaction order α to 1.
- 6 Solve the problem again with the new reaction order by clicking the **Estimate Parameters** button.
- 7 Continue in the same manner to produce results for $\alpha = 2$.

Microbial Growth in Food

Introduction

Predicting levels of disease-producing microorganisms has enormous cost-saving potential in food product development. Accurate models reduce the need for extensive and time-consuming microbiological testing. Furthermore, food processing methods may be re-evaluated, possibly leading to milder treatments of fresh foods while maintaining microbial safety.

In this example, you first set up a kinetic model of the microbial growth in the Reaction Engineering Lab and solve the corresponding material balance equations under isothermal conditions. Subsequently, you export the reaction model to COMSOL Script, where you perform a parametric study, observing bacterial growth as a function of temperature.

The model uses a chemical kinetics approach to describe the four phases of the microbial life cycle. The study specifically concerns the growth and death of *Staphylococcus aureus* in bread (Ref. 1). *S. aureus* is a dangerous pathogen that grows anaerobically and produces a heat-resistant and persistent toxin, causing cramps, diarrhoea, and nausea.

Model Description

Models of bacterial life cycles can be set up in a manner analogous to chemical reaction mechanisms. The four steps involved are represented in Figure 4-56.

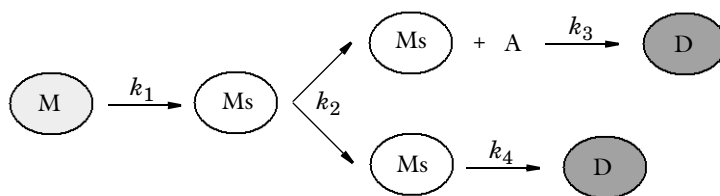


Figure 4-56: The life and death of *Staphylococcus aureus*.

The first step corresponds to the activation of cells from the lag phase (M) to the growth phase (Ms). The second step represents the multiplication of cells via binary division. This step also produces an antagonistic metabolite (A), which interacts with the active species (Ms) to cause cell death (D). The natural death of cells also occurs.

The four irreversible reactions illustrated in Figure 4-56 translate into the following reaction rate expressions:

$$r_1 = k_1 c_M \quad (4-97)$$

$$r_2 = k_2 c_{Ms} \quad (4-98)$$

$$r_3 = k_3 c_{Ms} c_A \quad (4-99)$$

$$r_4 = k_4 c_{Ms} \quad (4-100)$$

Making the use of these reaction rates and the reaction stoichiometry, the material balances for the model become:

$$\frac{dc_M}{dt} = -r_1 \quad (4-101)$$

$$\frac{dc_{Ms}}{dt} = r_1 + r_2 - r_3 - r_4 \quad (4-102)$$

$$\frac{dc_A}{dt} = r_2 - r_3 \quad (4-103)$$

$$\frac{dc_D}{dt} = r_3 + r_4 \quad (4-104)$$

The above reaction rate expressions and balance equations are automatically generated in the Reaction Engineering Lab; just type the corresponding chemical reaction formulas into the user interface. Material balances are solved at constant system temperature.

Experiments provide the following rate constants for a set of relevant temperatures:

T (°C)	k ₁ (s ⁻¹)	k ₂ (s ⁻¹)	k ₃ (conc ⁻¹ s ⁻¹)	k ₄ (s ⁻¹)
10	5.67·10 ⁻⁶	1.16·10 ⁻⁵	2.06·10 ⁻¹⁵	1.22·10 ⁻⁵
20	1.36·10 ⁻⁶	1.37·10 ⁻⁵	1.92·10 ⁻¹⁵	1.16·10 ⁻⁵
30	1.08·10 ⁻⁵	3.53·10 ⁻⁵	3.66·10 ⁻¹⁴	6.60·10 ⁻⁶
40	2.91·10 ⁻⁵	5.43·10 ⁻⁵	2.65·10 ⁻¹³	1.47·10 ⁻⁵

The temperature is given in degrees Celsius and the cell concentration in cell count per µL.

Results

Figure 4-57 shows the development of all species as a function of time at a system temperature of 40 °C. As experimental techniques of measuring *S. aureus* cells do not distinguish between cells in the lag phase (M) and the multiplying phase (Ms), the plot also shows the total cell count, $U = M + Ms$.

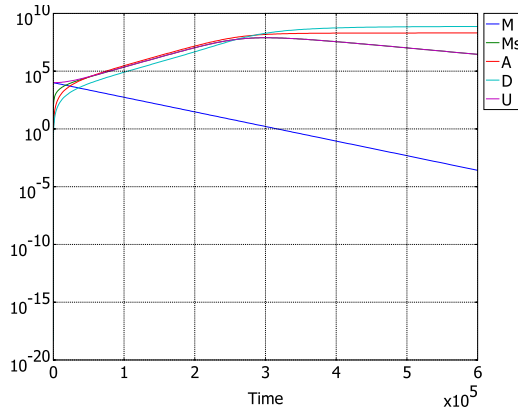


Figure 4-57: Growth and death of *S. aureus* in bread, at 40 °C, during a 7 day time span. Cell species concentrations given in (cell count μ/L) as functions of time (s).

Lag phase cells (M) undergo a first-order decline toward limiting values, while the antagonist (A) and the dead cells (D) show a first-order increase. The concentration of actively multiplying species (Ms) increases to a maximum and then declines. Excluding the initial stages of the simulation, the total number of living cells (U) is close to the amount of multiplying cells (Ms). This means that Ms plays the predominant role in determining the value of U throughout most of the kinetics process.

Figure 4-58 shows the multiplying cell concentration as a function of time for system temperatures of 10, 20, 30, and 40 °C.

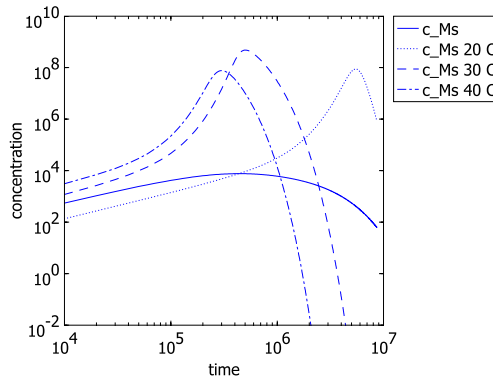


Figure 4-58: The concentration of multiplying *S. aureus* in bread, during a time span of 100 days, evaluated at temperatures of 10, 20, 30, and 40 °C. Cell species concentrations given in (cell count μL) as functions of time (s).

At 10 °C, there is a moderate increase of multiplying *S. aureus*. With increasing temperature, a distinct peak in cell concentration is established, occurring earlier in time, with increasing temperature. The maximum cell concentration is lower when the system temperature is 40 °C, compared to 30 °C. This is consistent with the optimal growth temperature for *S. aureus* being 37.5 °C.

Reference

I. i.A. Taub, F.E. Feeherry, E.W. Ross, K. Kustin, and C.J. Doona, *Journal of Food Science*, vol. 68, p. 2530, 2003.

Model Library path: Food_Processing/microbial_growth

Modeling Using COMSOL Reaction Engineering Lab

- 1 Start the Reaction Engineering Lab.
- 2 In the **Model Navigator**, click the **New** button.

OPTIONS AND SETTINGS

- 1 Choose **Model>Expressions**, then enter the following data:

NAME	EXPRESSION	DESCRIPTION
U	$c_M + c_{Ms}$	Total living cell concentration

- 2 Click **OK**.

REACTIONS INTERFACE

- 1 Choose **Model>Reaction Settings** (or use the Main toolbar button).
- 2 Create four entries in the **Reaction selection** list by clicking the **New** button four times.
- 3 Enter the following reaction formulas by first selecting the appropriate row in the **Reaction selection** list and then typing the corresponding expression in the **Formula** edit field. Note how expressions for the reaction rates are automatically generated and presented in the **r** edit field.

REACTION ID #	REACTION FORMULA
1	$M \Rightarrow Ms$
2	$Ms \Rightarrow 2Ms + A$
3	$A + Ms \Rightarrow D$
4	$Ms \Rightarrow D$

- 4 In the **Reaction Settings** dialog box (the same as above), enter the forward rate constants by first selecting the appropriate row in the **Reaction selection** list, then deleting the default expression in the k^f edit field, and finally typing the following numbers for the different reactions:

REACTION ID #	k^f
1	$2.91e-5$
2	$5.43e-5$
3	$2.65e-13$
4	$1.47e-5$

SPECIES INTERFACE

- 1 Click the **Species** tab.
- 2 Check that the **Species selection** list has the four species (M, Ms, A, and D), given in the reaction formulas above.

- 3 On the **General** page, enter the following initial concentrations by selecting the species name in the **Species selection** list and typing in the corresponding value in the **c₀** edit field:

SPECIES	c ₀
M	1e4
Ms	0
A	0
D	0

Notice that the default value is zero, so you only have to specify those initial values that deviate from zero, in this case the value for M.

- 4 Click **Close** when you are finished.

COMPUTING THE SOLUTION

- 1 Choose **Simulation>Solver Parameters**.
- 2 Clear the **Stop if steady state is reached first** check box.
- 3 In the **Time stepping** area, type 0:1e4:7*24*3600 in the **Times** edit field. This results in a simulation from time zero to seven days of reaction.
- 4 Click **OK**.
- 5 Click the **Solve Problem** button (=) on the Main toolbar to compute the solution.

POSTPROCESSING AND VISUALIZATION

The default plot is a linear plot of all species concentrations as functions of time. To generate Figure 4-57, follow these steps:

- 1 Choose **Postprocessing>Plot Parameters** (or use the corresponding button on the Main toolbar).
- 2 From the **Predefined quantities** list, select **Total living cell concentration**.
- 3 Click the **Add Entered Expression** button (>) next to the **Expression** edit field below the **Predefined quantities** list to add **U** to the **Quantities to plot** list.
- 4 Click **OK**.
- 5 Click the **Y log** button on the Main toolbar.
- 6 Click the **Edit Plot** button on the Main toolbar to open the plot editor.
- 7 In the **Axis** tab, clear the **y limits: Auto** check box, and type 1e-4 and 1e10 in the corresponding edit fields.

8 Click **OK**.

Modeling Using COMSOL Script

The goal is to solve the reaction model for four different reaction conditions and then plot the solution for the active species, Ms, for all four cases.

EXPORT

In the Reaction Engineering Lab, choose

File>Export>REL Structure to Workspace as 'rel'.

COMSOL Script launches, if not already open.

SCRIPTING

1 Click the **COMSOL Script** window.

You can choose between using the ready-made script that comes with the model or typing it in yourself. If you choose to run the ready-made script, you can skip the next step, where the script is created and saved, and continue with Step 7.

2 Type edit at the prompt to bring up a **COMSOL Script Editor** window.

3 If you choose to type it in yourself, type the following script into the text editor:

```
% Create vectors for containing the forward rate constants
% for the different temperatures
k1 = [5.67e-6 1.36e-6 1.08e-5 2.91e-5];
k2 = [1.16e-5 1.37e-5 3.53e-5 5.43e-5];
k3 = [2.06e-15 1.92e-15 3.66e-14 2.65e-13];
k4 = [1.22e-5 1.16e-5 6.6e-6 1.47e-5];

linecolors = {'b','r','g','m'};

%create a loop
for i = 1:4
    % solve the reaction model
    rel.sol=femtime(rel, 'report','off', ...
        'solcomp',{'c_M','c_Ms','c_A','c_D'}, ...
        'outcomp',{'c_M','c_Ms','c_A','c_D'}, ...
        'const',{'kf_1',k1(i),'kf_2',k2(i),'kf_3',k3(i),'kf_4',k4(i)},
    ...
        'tlist',0:1e4:100*24*3600);

    %Plot the results for each simulation
    postglobalplot(rel,'c_Ms','axistype',{'log','log'}, ...
        'axis',[4 7 -2 10],'grid','off','linlegend','on', ...
        'axislabel',{'time','concentration'}, ...
        'lincolor',linecolors{i});
```

```
hold on;
```

```
end;
```

- 4 Choose **File>Save** to save the file and specify the name as: `microbial_growth.m`.
- 5 Go back to the COMSOL Script command window by clicking in it.
- 6 Run the script by choosing **File>Run M-file**. Browse to where you saved the file, select it, and click **Open**.
- 7 To run the ready-made script, choose **File>Run M-file**, browse to `models/Reaction_Engineering_Lab/Food Processing/microbial_growth.m` in the COMSOL installation directory, and click **Open**.
- 8 Click the **Edit Plot** button in the **Figure 1** window.
- 9 Select the first **Axes>Line(c_Ms)**.
- 10 In the **Legends** edit field, type `c_Ms 10 C`.
- 11 Select the second **Axes>Line(c_Ms)**.
- 12 In the **Legends** edit field, type `c_Ms 20 C`.
- 13 Select the third **Axes>Line(c_Ms)**.
- 14 In the **Legends** edit field, type `c_Ms 30 C`.
- 15 Select the fourth **Axes>Line(c_Ms)**.
- 16 In the **Legends** edit field, type `c_Ms 40 C`.
- 17 Click **OK**.

You should now get Figure 4-58.

Hydrocarbon Dehalogenation in a Tortuous Microreactor

Introduction

Removing halogen groups from hydrocarbons is an important reaction step in several chemical processes. One application is water purification. Other examples involve organic synthesis, where the removal of halogen groups serves as a starting point for carbon-carbon coupling reactions. Typically, the carbon-halogen bond scission is activated by precious metal catalysts based on platinum or palladium.

The model presented here shows hydrocarbon dehalogenation as it occurs in a microreactor. The reactants are transported from the fluid bulk to the catalytic surfaces at the reactor walls, where they react. A first model is set up in Reaction Engineering Lab, where two competing reactions are analyzed. Subsequently, the reaction kinetics are exported to the MEMS Module, where a space-dependent model of the microreactor is set up and solved.

Note: This model requires the COMSOL Reaction Engineering Lab and the MEMS Module.

Model Definition

The adsorption of halogenated hydrocarbons onto the surface of a platinum catalyst leads to cleavage of the carbon halogen bond. The hydrocarbon fragments then undergo either hydrogenation or coupling reactions. Figure 4-59 illustrates the overall reactions for a brominated hydrocarbon species.

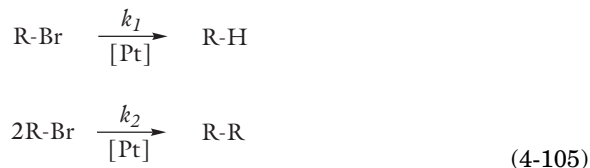


Figure 4-59: The dehalogenation of RBr can result either in hydrogenation or coupling of the hydrocarbon fragments.

The reaction rates are:

$$r_1 = k_1 c_{RB} r \quad (4-106)$$

and

$$r_2 = k_2 c_{RB}^2 r \quad (4-107)$$

where the rate constants are given by the Arrhenius expression:

$$k_j = A_j \exp\left(-\frac{E_j}{R_g T}\right) \quad (4-108)$$

In Equation 4-108, A is the frequency factor, and E the activation energy (J/mol). The table below lists the values of the Arrhenius parameters for the two reactions.

TABLE 4-2: ARRHENIUS PARAMETERS

	FREQUENCY FACTOR	ACTIVATION ENERGY
Reaction 1	2e-3	10e3
Reaction 2	1e-3	30e3

IDEAL REACTOR MODEL

The mass balance equation for a flow-through reactor is given by

$$\frac{dF_i}{dV} = R_i \quad (4-109)$$

where F is the molar flow rate (mol/s), V the reactor volume (m³), and R_i the net reaction term (mol/(m³·s)). If the reactor has constant cross-section and constant flow velocity, the left hand side of Equation 4-109 can be rewritten as

$$\frac{dF_i}{dV} = u \frac{dc_i}{dx} = \frac{dc_i}{d\tau} \quad (4-110)$$

The reactor mass balance thus becomes

$$\frac{dc_i}{d\tau} = R_i \quad (4-111)$$

where τ represents the residence time (s). The assumption of constant flow velocity is valid for incompressible liquids or liquids where the effect of temperature on the density is small. Equation 4-111 is identical to the balance equation of the batch

reactor, except that residence time replaces the reaction time. You can therefore make use of the Batch reactor type when solving the model in the Reaction Engineering Lab.

The ideal reactor model assumes by default that reactions take place in the entire reactor volume. In the 3D microreactor model, reactions occur at catalytic surfaces located at the reactor walls. In order to make the ideal model represent a reactor with surface reactions, Equation 4-111 has to be scaled by the reactive area per reactor volume. Scaling the ideal reactor equations by the dimensions of the microreactor makes the 1D and 3D models comparable. The area to volume ratio is

$$\frac{WL}{WLH} = \frac{1}{H} \quad (4-112)$$

where W is the width of the channel (m), H the channel height (m), and L the length of a reactive section (m). The scaled ideal reactor equation is then

$$\frac{dc_i}{d\tau} = \frac{R_i}{H} \quad (4-113)$$

Note that the net reaction term (R_i) in this case represents surface reactions ($\text{mol}/(\text{m}^2 \cdot \text{s})$).

SPACE-DEPENDENT MODEL

The microreactor considered in this example consists of a tortuous channel, fitted with inlet and outlet adapter sections, as illustrated in Figure 4-60.

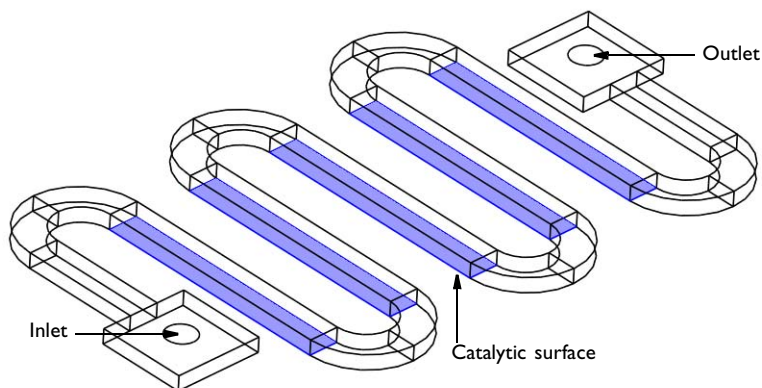


Figure 4-60: Microreactor geometry.

In the straight sections of the reactor, the channel walls are in part coated with platinum catalyst. As water with small amounts of a brominated hydrocarbon flows through the reactor, dehalogenation reactions occur at the catalytic surfaces.

MOMENTUM BALANCES

The flow in the channel is described by the Navier-Stokes equations:

$$\begin{aligned} \nabla \cdot [-\eta(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) + p\mathbf{I}] &= -\rho(\mathbf{u} \cdot \nabla)\mathbf{u} \\ \nabla \cdot \mathbf{u} &= 0 \end{aligned} \quad (4-114)$$

where ρ denotes density (kg/m^3), \mathbf{u} represents the velocity (m/s), η denotes viscosity ($\text{kg}/(\text{m} \cdot \text{s})$), and p equals pressure (Pa).

A pressure difference drives the flow through the reactor, as indicated by the boundary conditions

$$\begin{aligned} p &= p_{\text{inlet}} && \text{inlet} \\ p &= 0 && \text{outlet} \end{aligned} \quad (4-115)$$

Each pressure condition is specified along with a vanishing viscous stress condition at the boundary

$$\eta(\nabla \mathbf{u} + (\nabla \mathbf{u})^T)\mathbf{n} = \mathbf{0}$$

At the wall the velocity is zero

$$\mathbf{u} = \mathbf{0} \quad \text{walls} \quad (4-116)$$

MASS BALANCES

The mass balances set up and solved are the diffusion-convection equations at steady state:

$$\nabla \cdot (-D_i \nabla c_i + c_i \mathbf{u}) = 0 \quad (4-117)$$

where D_i denotes the diffusion coefficient (m^2/s), c_i is the species concentration (mol/m^3), and \mathbf{u} equals the velocity vector (m/s).

No reactions take place in the fluid bulk. Rather, the reactions take place on the catalytic surfaces. The boundary fluxes at the catalytic surfaces thus become

$$\mathbf{n} \cdot (-D_i \nabla c_i + c_i \mathbf{u}) = R_i \quad (4-118)$$

where R_i represents the reaction term. Note that these boundary conditions are set up automatically as you export the reaction kinetics from the Reaction Engineering Lab to COMSOL Multiphysics.

Inlet conditions are equal to the inlet concentrations

$$c = c_{\text{in}} \quad (4-119)$$

At the outlet, you can set the convective flux condition, assuming that the transport of mass across the boundary is dominated by convection

$$\mathbf{n} \cdot (-D\nabla c) = 0 \quad (4-120)$$

All other boundaries use the insulating condition

$$\mathbf{n} \cdot (-D\nabla c + c\mathbf{u}) = 0 \quad (4-121)$$

Results

First review the results of the ideal reactor model, which you set up and solve in the Reaction Engineering Lab.

Figure 4-61 through Figure 4-63 show concentration profiles of reactant and products as function of residence time, evaluated at 288 K, 343 K, and 363 K.

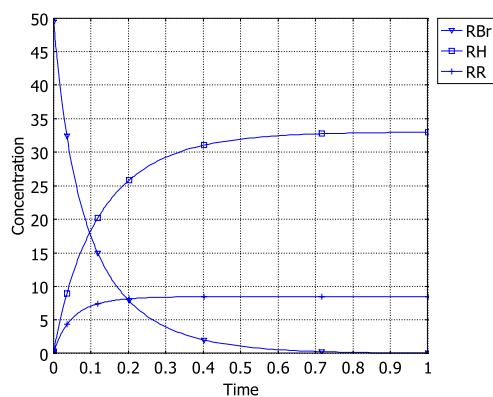


Figure 4-61: Concentration of the RBr, RH, and RR species as function of residence time. Reactions occur at 288 K.

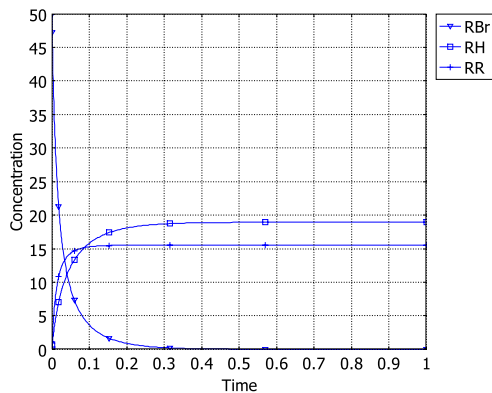


Figure 4-62: Concentration of the RBr, RH, and RR species as function of residence time. Reactions occur at 343 K.

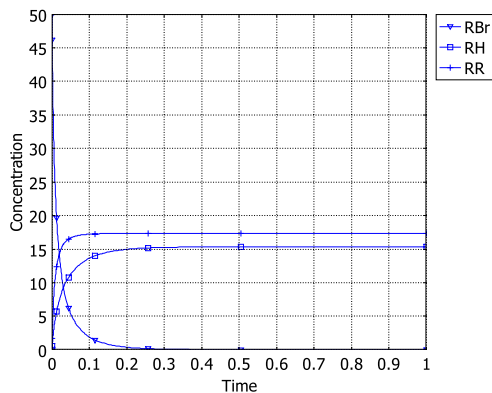


Figure 4-63: Concentration of the RBr, RH, and RR species as function of residence time. Reactions occur at 363 K.

The hydrocarbon coupling reaction has the higher activation energy and is hence more temperature sensitive than the hydrogenation reaction (see Table 4-2). The concentration plots of the ideal reactors outline the effect quite clearly. At 288 K, the hydrogenation product RH is dominant, while at 363 K the coupling product is the more prominent. Notably, at 343 K, the concentration dependency on the reaction rates becomes accentuated, so that RBr dominates only at shorter τ and RH at longer τ .

Although the primary goal may be to remove the halogenated reactant, RBr, it may also be important to set reaction conditions in such a way that the most favorable by-product is formed. The present model shows how such design aspects can readily be investigated in the Reaction Engineering Lab.

The next set of results refer to the space-dependent model of a tortuous microreactor, set up and solved in COMSOL Multiphysics.

Figure 4-64 shows the velocity of the laminar flow field in the reactor. The flow is driven by a pressure difference of 1500 Pa between inlet and outlet. The resulting maximum velocity is close to 5 mm/s.

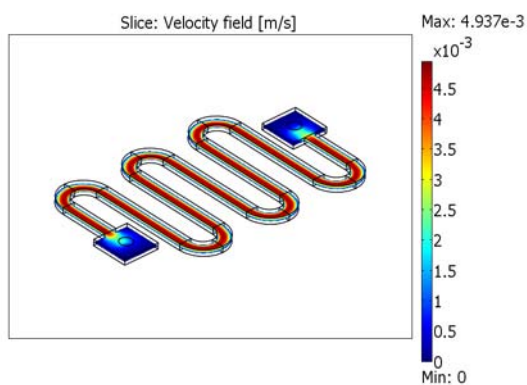


Figure 4-64: Velocity field in the reactor where the pressure difference between inlet and outlet is 1500 Pa.

Figure 4-65 shows the concentration distribution of the reactant RBr in the reactor. At relatively low temperature, 288 K, the outlet concentration is 10.6 mol/m³.

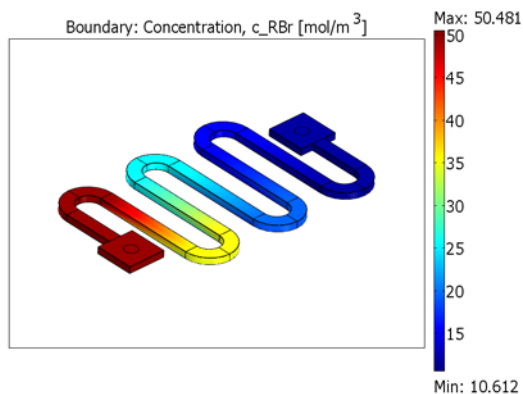


Figure 4-65: Concentration distribution of the halogenated reactant RBr. Fluid properties and reaction rates are evaluated at 288 K.

Running the reactor at 363 K, the outlet concentration of RBr is still 6.7 mol/m³.

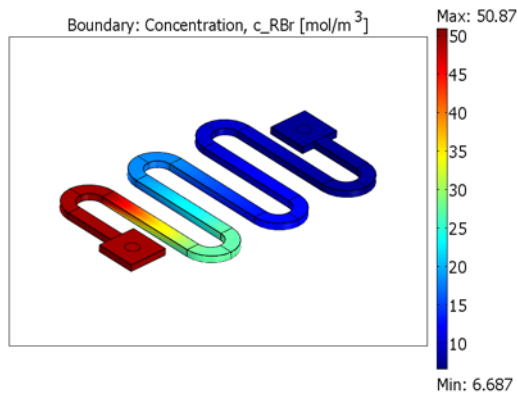


Figure 4-66: Concentration distribution of the halogenated reactant RBr. Fluid properties and reaction rates are evaluated at 363 K.

Judging from the results of the ideal reactor models, a more pronounced temperature effect would be expected. The reason for this apparently moderate influence on conversion is that the increased temperature also affects the flow.

Raising the temperature from 282 K to 363 K decreases the viscosity of water from $1.36 \cdot 10^{-3}$ to $3.17 \cdot 10^{-4}$. This is automatically taken into account by the temperature dependent fluid properties. As the flow through the reactor is driven by a constant pressure difference, the velocity will increase as viscosity decreases. Results show that the maximum fluid velocity at 363 K is ~3.6 times greater than at 282 K, resulting in a shorter residence time.

Model Library path: Microfluidics/tortuous_reactor

The following path shows the location of the COMSOL Multiphysics model:

Model Library path: Reaction_Engineering_Lab/Microfluidics/
tortuous_reactor

Modeling Using COMSOL Multiphysics

MODEL NAVIGATOR

- 1 Start COMSOL Multiphysics by clicking the desktop icon.
- 2 Select **3D** from the **Space dimension** list.
- 3 In the list of application modes select **MEMS Module>Microfluidics>Incompressible Navier-Stokes**.
- 4 Click **OK**.

GEOMETRY MODELING

Select the menu item **File>Import CAD Data From File**. Browse to the file `tortuous_reactor.mphbin` and click **Import**.

PHYSICS SETTINGS

Subdomain Settings—Incompressible Navier-Stokes

- 1 Choose **Physics>Subdomain Settings**.
- 2 In the **Subdomain selection** list, select all subdomains by pressing Ctrl+A and clicking the list.
- 3 Go to the **Material/Coefficients Library** by clicking the **Load** button.

- 4 Browse to **Liquids and Gases>Liquids>Water, liquid** and click **OK** to load the properties.
- 5 Click **OK**.

Boundary Conditions—Incompressible Navier-Stokes

- 1 Choose **Physics>Boundary Settings**.
- 2 Enter the following boundary conditions:

SETTINGS	BOUNDARY 6	BOUNDARY 104
Boundary type	Inlet	Outlet
Boundary condition	Pressure, no viscous stress	Pressure, no viscous stress
P_0	delta_p	0

Leave all other boundaries at their default setting (Wall, No slip).

- 3 Click **OK**.

OPTIONS AND SETTINGS

- 1 Choose **Options>Constants** then enter the following data:

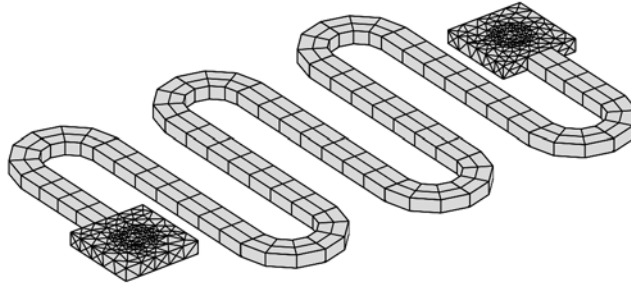
NAME	EXPRESSION	DESCRIPTION
delta_p	1.5[kPa]	Inlet overpressure
T	288[K]	Temperature

- 2 Click **OK**.

MESH GENERATION

- 1 Select the menu item **Mesh>Free Mesh Parameters**.
- 2 On the **Global** page select **Finer** from the **Predefined mesh sizes** list.
- 3 Click the **Boundary** page, select Boundary 8, and click the **Mesh Selected** button.
- 4 Choose **Mesh>Swept Mesh Parameters**.
- 5 Select Subdomains 2–19 and 21 from the **Subdomain selection** list by pressing Ctrl and clicking the list.
- 6 Click the **Mesh Selected** button.
- 7 Click **OK** to close the **Swept Mesh Parameters** dialog.
- 8 Go to the **Free Mesh Parameters** dialog, and click the Subdomain page.
- 9 Select Subdomains 1 and 20 from the **Subdomain selection** list by pressing Ctrl and clicking the list.

- 10 Click the **Mesh Selected** button.
- 11 Click **OK** to close the **Free Mesh Parameters** dialog box.



COMPUTING THE SOLUTION

- 1 Solve the problem by clicking the **Solve** button (=) on the Main toolbar.
- 2 Select the menu item **Solve>Solver Manager**.
- 3 Press the **Store Solution** button and the click **OK**.

POSTPROCESSING THE SOLUTION

The following steps reproduce Figure 4-64:

- 1 Choose **Postprocessing>Plot Parameters**.
- 2 On the **Slice** page, select the **Slice plot** check box.
- 3 Type 0 in the **x-levels** edit field and 1 in the **z-levels** edit field.
- 4 Click **OK**.

Modeling Using the COMSOL Reaction Engineering Lab

- 1 In the main user interface of COMSOL Multiphysics, choose **File>Reaction Engineering Lab**.

The main user interface of COMSOL Reaction Engineering Lab opens up.

- 2 Click the **COMSOL Reaction Engineering Lab** window.

OPTIONS AND SETTINGS

- 1 Click the **Model Settings** button on the Main toolbar.
- 2 On the **General** page type 288 in the **Temperature** edit field.

3 Click **Close**.

4 Choose **Model>Constants** then enter the following data:

NAME	EXPRESSION	DESCRIPTION
H	5e-6	Reactor channel height (m)

5 Click **OK**.

REACTIONS INTERFACE

1 Click the **Reaction Settings** button on the Main toolbar.

2 Make sure the **Reactions** page is active. Create two entries in the **Reaction selection** list by clicking the **New** button twice.

3 Enter the following reaction formulas by first selecting the appropriate row in the **Reaction selection** list and then entering the corresponding text in the **Formula** edit field.

REACTION ID #	REACTION FORMULA
1	$\text{RBr} \rightarrow \text{RH}$
2	$2\text{RBr} \rightarrow \text{RR}$

4 Select row 1 from the **Reaction selection** list.

5 Select the **Use Arrhenius expression** check box.

6 Enter $2\text{e-}3$ in the **A** edit field and $10\text{e}3$ in the **E** edit field.

7 Select row 2 from the **Reaction Selection** list.

8 Select the **Use Arrhenius expression** check box.

9 Enter $1\text{e-}1$ in the **A** edit field and $30\text{e}3$ in the **E** edit field.

10 Select Reaction 1 from the **Reaction selection** list and type $k_{f_1} \cdot c_{\text{RBr}}/H$ in the **r** edit field.

11 Select Reaction 2 from the **Reaction selection** list and type $k_{f_2} \cdot c_{\text{RBr}}^2/H$ in the **r** edit field.

You have now modified the automatically generated reaction rates by dividing with the scale factor H, according to Equation 4-113.

SPECIES INTERFACE

1 Click the **Species** tab.

2 Select **RBr** from the **Species selection** list and type 50 in the **c₀** edit field.

3 Click **Close**.

COMPUTING THE SOLUTION

- 1 Open the **Simulation>Solver Parameters** dialog box.
- 2 Type 1 in the **Times** edit field.
- 3 Click **OK**.
- 4 Click the **Solve Problem** button (=) on the Main toolbar.

POSTPROCESSING AND VISUALIZATION

The results of Figure 4-61 are shown in the default plot. To generate the results shown in Figure 4-62 follow these steps.

- 1 Click the **Model Settings** button on the Main toolbar.
- 2 On the **General** page type 343 in the **Temperature** edit field.
- 3 Click **Close**.
- 4 Click the **Solve Problem** button.

To generate the results shown in Figure 4-63:

- 1 Click the **Model Settings** button on the Main toolbar.
- 2 On the **General** page type 363 in the **Temperature** edit field.
- 3 Click **Close**.
- 4 Click the **Solve Problem** button.

EXPORT SETTINGS

You will now proceed to export the reaction kinetics to the reacting boundaries in the Multiphysics model. Recall that the rate constants are temperature dependent. To export a temperature variable while only exporting mass balances, follow these steps:

- 1 Click the **Model Settings** button on the Main toolbar.
- 2 On the **General** page type Temp in the **Temperature** edit field.
- 3 Click **Close**.

This will export a variable name Temp rather than a constant temperature, which would otherwise be the case.

Recall also that the reaction rates were scaled in order to make the 1D ideal reactor comparable to the 3D microreactor. As you are about to export the reaction kinetics to the 3D model, the effect of the scaling should first be removed.

1 Choose **Model>Constants** then set the scaling factor H to 1:

NAME	EXPRESSION	DESCRIPTION
H	1	reactor channel height (m)

2 Click **OK**.

Now, move on to export the reaction model.

- 1 Click the **Export to COMSOL Multiphysics** button on the Main toolbar.
- 2 The **Export to COMSOL Multiphysics** dialog box appears.
- 3 Select **Boundary** in the **Domain level** drop down list.
- 4 Go to the **Export mass balance** area, and in the **Application mode** list select **Convection and Diffusion: New**.
- 5 In the **Group name** edit field type reactions.
- 6 Move to the **Export energy balance** area and clear the check box in the upper left corner.
- 7 Click the **Export** button at the bottom of the dialog box.

Modeling Using COMSOL Multiphysics

It is now time to investigate the chemistry taking place in a space-dependent model.

Click the **COMSOL Multiphysics** window.

Subdomain Settings—Convection and Diffusion

- 1 From the **Multiphysics** menu select **Convection and Diffusion (chcd)**.
- 2 From the **Physics** menu select **Subdomain Settings**.
- 3 In the **Subdomain selection** list, select all subdomains by pressing Ctrl+A and clicking the list.
- 4 On the **c_RBr** page type the following:

EDIT FIELD	VALUE
Diffusion coefficient	D
x-velocity	u
y-velocity	v
z-velocity	w

- 5 Type in the same entries on the **c_RH** page and the **c_RR** page.

6 Click **OK**.

Boundary Conditions—Convection and Diffusion

1 From the **Physics** menu select **Boundary Settings**.

2 In the **Boundary selection** list, select **27**, **41**, **57**, **71**, and **87** by pressing Ctrl and clicking the entries. These boundaries represent the reactive surfaces.

3 Select **reactions** from the **Group** list.

This associates the exported kinetics from Reaction Engineering Lab with the catalytic surfaces. The **Flux** boundary condition is automatically set on all mass balance pages, and the appropriate reaction terms appear in the **Inward flux** edit fields.

4 Enter the remaining boundary conditions for each of the species **c_RBr**, **c_RH**, and **c_RR** according to the following table:

SETTINGS	BOUNDARY 6	BOUNDARY 104	ALL OTHERS
Boundary condition	Concentration	Convective flux	Insulation/Symmetry
c_RBr ₀	50		
c_RH ₀	0		
c_RR ₀	0		

5 Click **OK**.

OPTIONS AND SETTINGS

1 From the **Options** menu select **Constants**.

2 Add entries to complete the list of constants as follows:

NAME	EXPRESSION	DESCRIPTION
delta_p	1.5[kPa]	Inlet overpressure
T	288[K]	Temperature
D	1e-6[m^2/s]*exp(-2000[K]/T)	Diffusivity
Temp	T	Temperature

3 Click **OK**.

COMPUTING THE SOLUTION

1 Select the menu item **Solve>Solver Manager**.

- 2 In the **Values of variables not solved for and linearization point**, click the **Stored solution** option button.
- 3 Click the **Solve For** tab.
- 4 Select only the **Convection and Diffusion (chcd)** folder in the **Solve for variables** tree.
- 5 Click **OK**.
- 6 Solve the problem by clicking the **Solve** button (=) on the Main toolbar.

POSTPROCESSING THE SOLUTION

The following steps reproduce Figure 4-65:

- 1 Choose **Postprocessing>Plot Parameters**.
- 2 On the **Boundary** page, select the **Boundary plot** check box.
- 3 Type c_{RBr} in the **Expression** edit field.
- 4 Click **OK**.

To reproduce the results in Figure 4-66, change the variable T in the **Constants** dialog box to 363[K], and solve for the flow and mass balances as outlined above.

Ibuprofen Synthesis

Introduction

Kinetic analysis of catalytic reactions is essential for understanding rate behavior as well as the reaction mechanism. Developing knowledge of intrinsic reaction kinetics and of rate equations is central to reaction engineering studies aimed at improving reactor design.

This example illustrates the reaction kinetics of a complex chemistry occurring in a perfectly stirred tank reactor. The homogeneous catalysis of 1-(4-isobutylphenyl) ethanol into the anti-inflammatory drug ibuprofen serves as the example chemistry. The model determines concentrations of reactants, intermediates, and products as functions of time for the network of chemical reactions.

The chemistry in this example involves homogeneous catalysis. As this terminology suggests, the catalyst and the reacting species are in the same phase. Most commonly, a liquid reaction mixture contains a soluble metalorganic complex that affects the catalysis. Organometallic catalysts can often be fine-tuned with respect to reaction activity and selectivity. Because these relatively expensive catalysts produce highly-refined reaction products, they commonly find application in fine chemicals or pharmaceuticals.

The model focuses on the use of the Reaction Engineering Lab for a kinetics investigation. You easily enter chemical reaction formulas from the keyboard, then the Reaction Engineering Lab automatically generates rate expressions and material balances. It solves the equations, and you postprocess results directly in the graphical user interface.

Model Description

Analyzing chemical kinetics involves solving the set of ordinary differential equations corresponding to individual steps in a network of reactions. This example illustrates the

kinetics of ibuprofen synthesis. Figure 4-67 shows the reaction steps displayed in a catalytic cycle (Ref. 1).

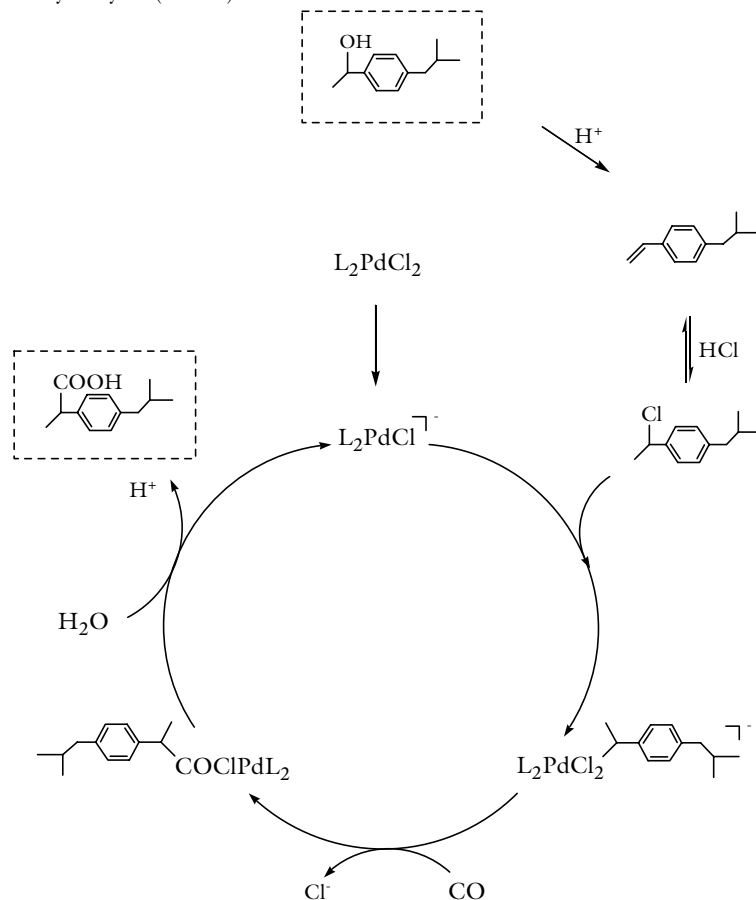
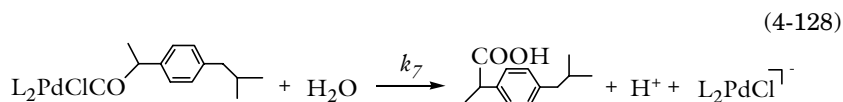
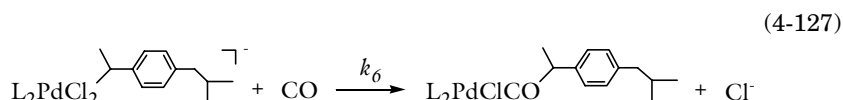
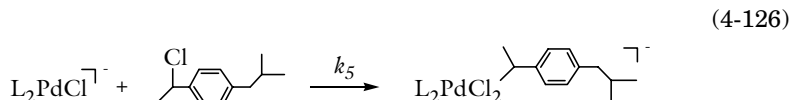
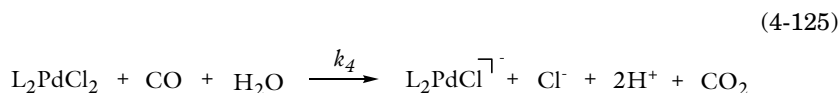
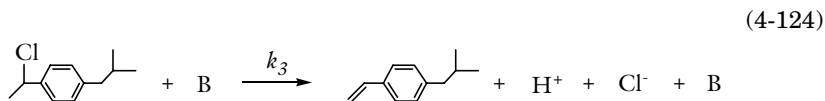
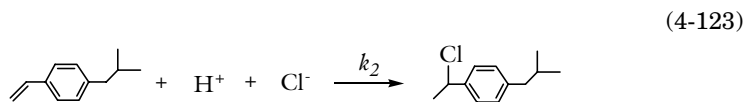
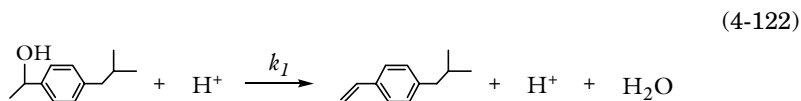


Figure 4-67: Catalytic cycle of ibuprofen synthesis.

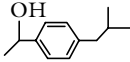
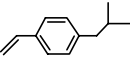
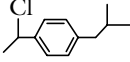
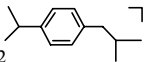
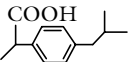
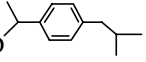
Prior to entering the cycle, the starting material, 1-(4-isobutylphenyl)ethanol, is first dehydrated to form 4-isobutylstyrene. This species subsequently undergoes the addition of HCl to produce the active substrate 1-(4-isobutylphenyl)ethyl chloride. The palladium catalyst must also go through an initial transformation, from L_2PdCl_2 (L =triphenylphosphine) to anionic L_2PdCl , before becoming active. The activated catalyst then assists in the carbonylation and hydrolysis of 1-(4-isobutylphenyl)ethyl chloride, producing ibuprofen.

The following reactions represent the catalytic cycle:



Reaction 4-122 involves the dehydration of the reactant alcohol to form the corresponding alkene. Reaction 4-123 describes the hydrohalogenation of alkene, resulting in the active substrate 1-(4-isobutylphenyl)ethyl chloride. Reaction 4-124 shows the dehydrohalogenation of the active substrate, assisted by a base, B. Reaction 4-125 describes the transformation of the pre-catalytic species L_2PdCl_2 into the active anionic catalyst $\text{L}_2\text{PdCl}^{\ominus}$. In Reaction 4-126 the active substrate undergoes oxidative addition to the $\text{L}_2\text{PdCl}^{\ominus}$ catalyst. Reaction 4-127 summarizes the carbonylation, and Reaction 4-128 describes the hydrolysis of the metalorganic species, leading to the formation of ibuprofen and regeneration of the catalyst.

In order to make species notation more manageable, this example uses the following labels:

species	abbreviation	species	abbreviation
	roh	L_2PdCl_2	pd1
	ren	L_2PdCl^{\ominus}	pd2
	rhcl	L_2PdCl_2 	pd3
	ibu	$L_2PdClCO$ 	pd4

Making use of this notation, the reaction rates corresponding to Reaction 4-122 through Reaction 4-128 are:

$$r_1 = k_1 c_{roh} c_h \quad (4-129)$$

$$r_2 = k_2 c_{ren} c_h c_{cl} \quad (4-130)$$

$$r_3 = k_3 c_{rhcl} c_b \quad (4-131)$$

$$r_4 = k_4 c_{pd1} c_{co} c_{h2o} \quad (4-132)$$

$$r_5 = k_5 c_{pd2} c_{rhcl} \quad (4-133)$$

$$r_6 = k_6 c_{pd3} c_{co} \quad (4-134)$$

$$r_7 = k_7 c_{pd4} c_{h2o} \quad (4-135)$$

The Reaction Engineering Lab automatically generates these expressions and displays them immediately when you enter the chemical reaction formulas. By default, the

software assumes that the chemistry takes place isothermally in a perfectly stirred batch reactor.

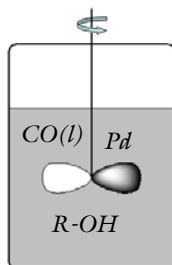


Figure 4-68: A perfectly stirred batch reactor where the reactant alcohol is carbonylated to form ibuprofen by means of palladium catalysis.

With no inflow or outflow from the reactor, the change of species concentrations with time is a function only of the reaction rates. The following set of ODEs result from the reaction rates (Equation 4-129 to Equation 4-135) and stoichiometry of the reaction formulas (Equation 4-122 to Equation 4-128):

$$\frac{dc_{roh}}{dt} = r_1 \quad (4-136)$$

$$\frac{dc_{ren}}{dt} = r_1 - r_2 + r_3 \quad (4-137)$$

$$\frac{dc_{rhl}}{dt} = r_2 - r_3 - r_5 \quad (4-138)$$

$$\frac{dc_{ibu}}{dt} = r_7 \quad (4-139)$$

$$\frac{dc_{pd1}}{dt} = -r_4 \quad (4-140)$$

$$\frac{dc_{pd2}}{dt} = r_4 - r_5 + r_7 \quad (4-141)$$

$$\frac{dc_{pd3}}{dt} = r_5 - r_6 \quad (4-142)$$

$$\frac{dc_{pd4}}{dt} = r_6 - r_7 \quad (4-143)$$

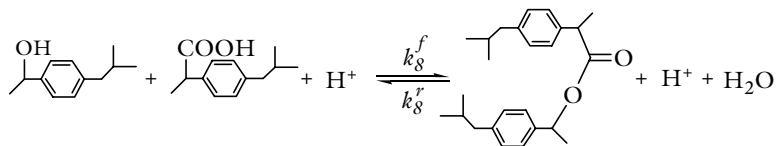
$$\frac{dc_h}{dt} = -r_2 + r_3 + 2r_4 + r_7 \quad (4-144)$$

$$\frac{dc_{cl}}{dt} = -r_2 + r_3 + r_4 + r_6 \quad (4-145)$$

$$\frac{dc_{h2o}}{dt} = r_1 - r_4 - r_7 \quad (4-146)$$

The Reaction Engineering Lab automatically generates and solves these equations.

The model investigates two reaction conditions. The first simulation (Case 1) solves Equation 4-136 to Equation 4-146. In Case 2 you subsequently modify the reaction network with an additional reaction, altering the simulation results. Assume that the reactant alcohol and product ibuprofen (a carboxylic acid) react reversibly, forming an ester:



The results of the two simulations are compared to gain insight in the process implications.

CASE I

Figure 4-69 shows the concentration profiles for selected reactants and products over time.

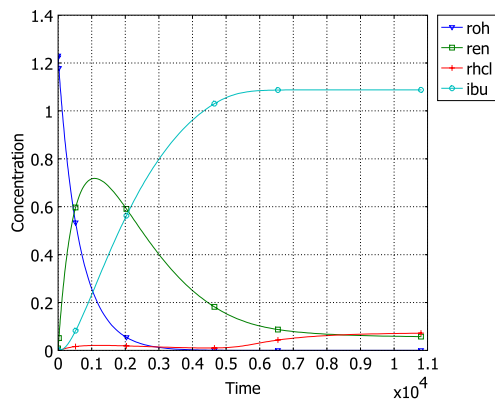


Figure 4-69: Selected species concentrations (mol/m³) as a function of time (s).

Clearly, after approximately 2 hours the process has run to completion.

CASE 2

This expansion of the original case adds a reversible reaction between the reactant alcohol and the product ibuprofen to form an ester. Figure 4-70 shows the concentration of ibuprofen and ester over time.

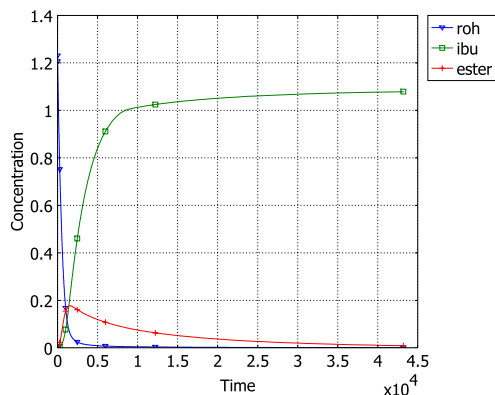


Figure 4-70: Selected species concentrations (mol/m^3) as a function of time (s).

In the course of the reaction, ester forms as an intermediary product. In order to achieve the same final concentration of ibuprofen for Case 2 as in Case 1, the process must run for at least 12 hours.

In conclusion, this example illustrates the use of the COMSOL Reaction Engineering Lab for analyzing the kinetics of a complex reaction network. When you enter the chemical-reaction formulas into the user interface, the Reaction Engineering Lab automatically sets up the corresponding rate expressions and material balances. You can modify simulation conditions effortlessly, for instance by activating/deactivating individual reactions or by changing initial conditions.

Reference

1. R.V. Chaudhari, A. Seayad, and S. Jayasree, *Catalysis Today*, vol. 66, p. 371, 2001.

Model Library path: Pharmaceuticals/ibuprofen_synthesis

MODEL NAVIGATOR—CASE I

- 1 Start the Reaction Engineering Lab.
- 2 In the **Model Navigator**, click the **New** button.

REACTIONS INTERFACE—CASE I

- 1 Click the **Reaction Settings** button on the Main toolbar.
- 2 Create seven entries in the **Reaction Selection** list by clicking the **New** button repeatedly.
- 3 Enter the following reaction formulas by first selecting the appropriate row in the **Reaction Selection** list and then typing the text in the **Formula** edit field. Note how the Reaction Engineering Lab automatically generates reaction rate expressions and presents them in the **r** edit field.

REACTION ID #	REACTION FORMULA
1	$\text{roh} + \text{h} \Rightarrow \text{ren} + \text{h}_2\text{o} + \text{h}$
2	$\text{ren} + \text{h} + \text{cl} \Rightarrow \text{rhcl}$
3	$\text{rhcl} + \text{b} \Rightarrow \text{ren} + \text{h} + \text{cl} + \text{b}$
4	$\text{pd}_1 + \text{co} + \text{h}_2\text{o} \Rightarrow \text{pd}_2 + \text{cl} + 2\text{h} + \text{co}_2$
5	$\text{pd}_2 + \text{rhcl} \Rightarrow \text{pd}_3$
6	$\text{pd}_3 + \text{co} \Rightarrow \text{pd}_4 + \text{cl}$
7	$\text{pd}_4 + \text{h}_2\text{o} \Rightarrow \text{pd}_2 + \text{h} + \text{ibu}$

- 4 Specify the forward rate constants, one by one, according to the table below by first selecting the appropriate row in the **Reaction selection** list and then typing the corresponding value in the **k^f** edit field.

REACTION ID #	k ^f
1	7.45e-3
2	1.25e-2
3	1.60e-3
4	1.50e-1
5	1.59
6	2.14e-1
7	9.52e-1

SPECIES INTERFACE—CASE I

- 1 Click the **Species** tab.
- 2 Check that the **Species selection** list has 14 entries when you have entered the reaction formulas just given.
- 3 On the **General** page, specify initial concentrations according to the table below by first selecting the appropriate entry in the **Species selection** list and then typing the corresponding value in the **c₀** edit field. (For species not in the table, keep the default value of **0** for **c₀**.)

SPECIES NAME	c ₀
roh	1.23
h	0.2
h2o	3
cl	0.2
b	0.1
pdl	1.21e-2
co	1.1

- 4 Click **Close**.

COMPUTING THE SOLUTION—CASE I

- 1 Choose **Simulation>Solver Parameters**.
- 2 In the **Time stepping** area, find the **Times** edit field and type 0 3600*3.
- 3 Click **OK**.
- 4 Click the **Solve Problem** button (=) on the Main toolbar.

POSTPROCESSING AND VISUALIZATION—CASE I

- 1 Choose **Postprocessing>Plot Parameters**.
- 2 Click the << button.
- 3 Go to the **Predefined quantities** list and Ctrl-click to select the entries **roh**, **ren**, **rhcl**, and **ibu**.
- 4 Click the > button to add the selected entries to the **Quantities to plot** list.
- 5 Click the **Line Settings** button, select the **Legend** check box, and click **OK**.
- 6 From the **Plot in** list, select **New figure**.
- 7 Click **OK** to generate Figure 4-69.

REACTIONS INTERFACE—CASE 2

- 1 From the **Model** menu, select **Reaction Settings**.
- 2 Click the **Reactions** tab.
- 3 Create a new entry in the **Reaction selection** list by clicking the **New** button.
- 4 Enter the following reaction formula by first selecting the appropriate row in the **Reaction selection** list and then typing the text in the **Formula** edit field:

REACTION ID #	REACTION FORMULA
8	ibu+roh+h<=>ester+h2o+h

- 5 Enter the corresponding forward and reverse rate constants by first selecting the appropriate row in the **Reaction selection** list and then entering the numbers in the k^f and k^r edit fields:

REACTION ID #	k^f	k^r
8	0.5	1e-2

SPECIES INTERFACE—CASE 2

- 1 Click the **Species** tab.
- 2 Notice that the **Species selection** list is updated with the new ester species. Its initial concentration is 0, the default value in the c_0 edit field.
- 3 Click **Close**.

COMPUTING THE SOLUTION—CASE 2

- 1 Choose **Simulation>Solver Parameters**.
- 2 In the **Time stepping** area, find the **Times** edit field and type 0 3600*12. Click **OK**.
- 3 Click the **Solve Problem** button on the Main toolbar.

POSTPROCESSING AND VISUALIZATION—CASE 2

- 1 Choose **Postprocessing>Plot Parameters**.
- 2 Remove the intermediate species **ren** and **rhcl** from the **Quantities to plot** list by Ctrl-clicking those entries and then clicking the **<** button.
- 3 From the **Predefined quantities** list, select the **ester** species. Add it to the **Quantities to plot** list by clicking the **>** button.
- 4 Select **Plot in** list and select **New figure**.
- 5 Click **OK** create Figure 4-70.

Protein Adsorption

This example uses algebraic equilibrium relations to model the time-dependent adsorption of proteins to an ion-exchanger medium. The fluid phase contains three components: two proteins and one salt. The adsorption/desorption kinetics are described by a set of equilibrium reactions where proteins displace ions adsorbed at the surface and vice versa.

The model highlights the implementation of reactions at chemical equilibrium in mass-transport modeling. Setting up the balance equations describing the present diffusion/reaction system results in a system of six partial differential equations. To include the algebraic equations describing reactions at chemical equilibrium, you must reformulate the system of balance equations. As this discussion illustrates, this reformulation process is normally quite involved—but it is important to note that the Reaction Engineering Lab automates this process. To include equilibrium reactions in your kinetics, simply enter the chemical reaction formulas and the corresponding equilibrium constants.

Introduction

The binding of proteins to ion exchangers can be described within the steric mass action approximation (SMA). This approach assumes that the adsorption of a protein can be considered as an exchange reaction of the protein with a given number of adsorbed ions.

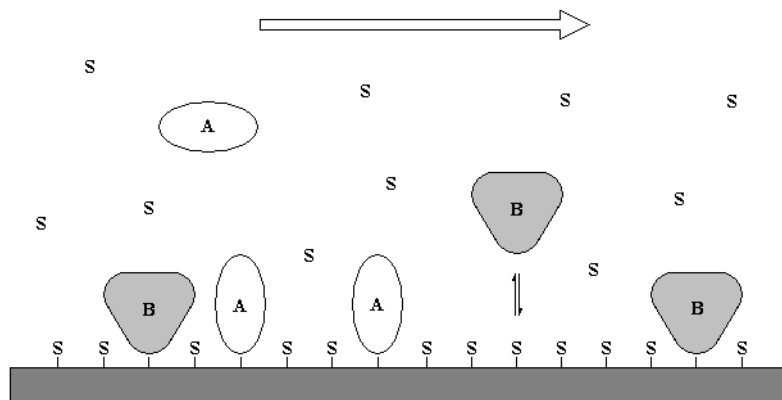
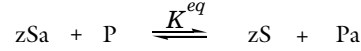


Figure 4-71: Proteins A and B displacing salt ions S at an ion-exchanger surface.

The equilibria describing the adsorption/desorption reactions are



Here, S denotes the salt ions, z represents the binding charge, P stands for the protein, and a indicates species being adsorbed to the surface. Once adsorbed, proteins can make neighboring salt ions unavailable for displacement, reducing the effective concentration of adsorbed salt ions, Sa . This fact is taken into account by a steric factor, σ , associated with each protein.

Assuming monovalent salt ions, the equilibrium expression for this reaction is

$$K^{eq} = \frac{c_{Pa}}{c_P} \left(\frac{c_S}{c_{Sa} - \sigma_P c_{Pa}} \right)^{|z|} \quad (4-147)$$

Model Definition

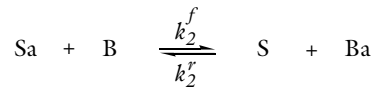
Two modeling assumptions are treated when studying the protein adsorption/desorption kinetics.

In the first instance, a perfectly mixed (space-independent) system is assumed. Initially, only free (S) and adsorbed (Sa) salt species are present. Equal concentrations of proteins A and B subsequently enter the system, as described by a Gaussian pulse:

$$c_i(t) = c_{i0} \exp(-(t - t_0)^2) \quad (4-148)$$

In the second instance, the influence of geometry is included. The modeling domain is a 1D representation of a section of a pore channel, 10 μm in length, in a particle of an ion exchanger gel. The channel is initially filled only with a salt solution, S . Proteins A and B subsequently enter the channel, diffuse along its length, and adsorb at the walls.

The following adsorption/desorption reactions occur:



In total, six species are involved: three in the liquid phase (c_S , c_A , and c_B) and three in the adsorbed phase (c_{Sa} , c_{Aa} , and c_{Ba}), all given in molar concentrations (mol/m³). The mass action law gives the reaction rates for reversible reactions as

$$r_1 = k_1^f c_{Sa} c_A - k_1^r c_S c_{Aa}$$

$$r_2 = k_2^f c_{Sa} c_B - k_2^r c_S c_{Ba}$$

The mass balances for the species in a time-dependent diffusion/reaction system are:

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (-D_A \nabla c_A) = -r_1 \quad (4-149)$$

$$\frac{\partial c_B}{\partial t} + \nabla \cdot (-D_B \nabla c_B) = -r_2 \quad (4-150)$$

$$\frac{\partial c_S}{\partial t} + \nabla \cdot (-D_S \nabla c_S) = r_1 + r_2 \quad (4-151)$$

$$\frac{\partial q_A}{\partial t} + \nabla \cdot (-D_{Aa} \nabla c_{Aa}) = r_1 \quad (4-152)$$

$$\frac{\partial q_B}{\partial t} + \nabla \cdot (-D_{Ba} \nabla c_{Ba}) = r_2 \quad (4-153)$$

$$\frac{\partial q_S}{\partial t} + \nabla \cdot (-D_{Sa} \nabla c_{Sa}) = -r_1 - r_2 \quad (4-154)$$

where D_i (m²/s) is the diffusion coefficient for species i in the liquid and adsorbed phase. In this system of mass balance equations, the actual forward and reverse reaction rates are not known. However, the relationship between the rates comes from the equilibrium relationship, Equation 4-147. Assuming that $z = 1$ and $\sigma_A = \sigma_B = 0$, the relationships are

$$K_1^{\text{eq}} = \frac{c_{Aa}}{c_A} \cdot \frac{c_S}{c_{Sa}}$$

$$K_2^{\text{eq}} = \frac{c_{Ba}}{c_B} \cdot \frac{c_S}{c_{Sa}}$$

In order to combine the information in the mass balances and the equilibrium expressions, you must form linear combinations of the former (Equation 4-149 to Equation 4-154), thereby removing reaction rates r_1 and r_2 from the equation system. An exemplary set of linear combinations produces the following system of equations to solve:

$$\frac{\partial}{\partial t}(c_S - c_{Aa} - c_{Ba}) + \nabla \cdot (-D_S \nabla c_S + D_{Aa} \nabla c_{Aa} + D_{Ba} \nabla c_{Ba}) = 0$$

$$\frac{\partial}{\partial t}(c_A + c_{Aa}) + \nabla \cdot (-D_A \nabla c_A - D_{Aa} \nabla c_{Aa}) = 0$$

$$\frac{\partial}{\partial t}(c_B + c_{Ba}) + \nabla \cdot (-D_B \nabla c_B - D_{Ba} \nabla c_{Ba}) = 0$$

$$\frac{\partial}{\partial t}(c_{Sa} + c_{Aa} + c_{Ba}) + \nabla \cdot (-D_{Sa} \nabla c_{Sa} - D_{Aa} \nabla c_{Aa} - D_{Ba} \nabla c_{Ba}) = 0$$

$$K_1^{\text{eq}} c_A c_{Sa} - c_{Aa} c_S = 0$$

$$K_2^{\text{eq}} c_B c_{Sa} - c_{Ba} c_S = 0.$$

The Reaction Engineering Lab automates this elimination procedure for reactions at equilibrium; it requires only the chemical reaction formula and the equilibrium constant. In this example $K_1^{\text{eq}} = 2$ and $K_2^{\text{eq}} = 5$.

Results

Figure 4-72 shows the concentrations of reacting species as function of time, assuming a perfectly mixed system.

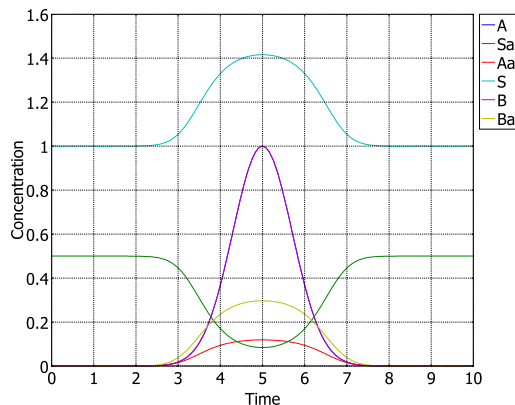


Figure 4-72: Concentrations (mol/m^3) of the reacting species as functions of time (s).

Initially, only salt species S and Sa are present, as is reasonable for a fresh ion exchanger medium. Proteins A and B enter the system in gaussian pulses centered around 5 seconds (the two concentration profiles overlap). The stronger adsorption affinity of protein B compared to protein A is readily observed. Note also how the concentration of free salt species S increases as the proteins adsorb at the surface. Towards the end of the time interval, all protein has been removed by eluent and the exchanger medium has been restored.

Figure 4-73 shows the results of the space-dependent model. Plotted are the concentrations of surface species as a function of time at a point located at the center of the geometry.

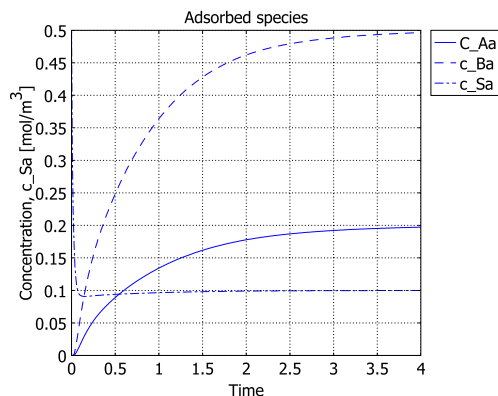


Figure 4-73: Adsorbed species concentrations of Aa, Ba, and Sa over time.

As the front of diffusing proteins moves through the pore section, proteins clearly displace salt as adsorbed species. The results once again reproduce the fact that protein *B* has a higher adsorption affinity compared to *A* as expected through the input specification of $K_2^{\text{eq}} > K_1^{\text{eq}}$.

In summary, the model shows how to quickly set up and solve an applied problem involving mass transport and reactions at chemical equilibrium. It is very easy to set up the equilibrium kinetics in the Reaction Engineering Lab by supplying the chemical reaction formulas and the equilibrium constants. Exporting the model to COMSOL Multiphysics allows you to study how a geometry affects the reacting system.

Model Library path: Pharmaceuticals/protein_adsorption1

Model Library path: Pharmaceuticals/protein_adsorption2

The following path shows the location of the COMSOL Multiphysics model:

Model Library path:

Reaction_Engineering_Lab/Pharmaceuticals/protein_adsorption2

Modeling Using COMSOL Reaction Engineering Lab

MODEL NAVIGATOR

- 1 Start the Reaction Engineering Lab.
- 2 In the **Model Navigator**, click the **New** button to launch the main user interface.
- 3 Click the **Reaction Settings** button on the Main toolbar.

OPTIONS AND SETTINGS

- 1 Click the **Model Settings** button on the Main toolbar.
- 2 Select the **Calculate thermodynamic properties** check box.
- 3 Select the **Calculate species transport properties** check box.
- 4 Click **Close**.

REACTIONS INTERFACE

- 1 Make sure that the **Reactions** page is active. Create two entries in the **Reaction selection** list by clicking the **New** button twice.
- 2 Enter the following reaction formulas by first selecting the appropriate row in the **Reaction selection** list and then typing the corresponding text in the **Formula** edit field:

REACTION ID #	REACTION FORMULA
1	$A + Sa = Aa + S$
2	$B + Sa = Ba + S$

- 3 Enter the following equilibrium constants by first selecting the appropriate row in the **Reaction selection** list and then typing the corresponding number in the **K^{eq}_0** edit field:

REACTION ID #	K^{eq}_0
1	2
2	5

SPECIES INTERFACE

- 1 Click the **Species** tab.
- 2 Check that the **Species selection** list has the six entries expected from entering the reaction formulas just given.
- 3 On the **General** page, for each species in the table below, select the entry in the **Species selection** list and then enter the corresponding value for the **Initial concentration** in the c_0 edit field.

SPECIES NAME	c_0
A	$\exp(- (t-5)^2)$
Sa	0.5
Aa	0
S	1
B	$\exp(- (t-5)^2)$
Ba	0

- 4 Select species **A** in the **Species selection** list and select the **Lock concentration/activity** check box.
- 5 Select species **B** in the **Species selection** list and select the **Lock concentration/activity** check box.
- 6 Go to the **Transport** page. For each species in the table below, select the entry in the **Species selection** list, select the **Specify diffusivity** check box, and enter the corresponding value for the **Diffusivity** in the D^0 edit field.

SPECIES NAME	D^0
A	5e-11
Sa	2e-9
Aa	1e-11
S	1e-8
B	7e-11
Ba	1.4e-11

- 7 Click **Close**.

MODEL SETTINGS

- 1 Click the **Model Settings** button on the Main toolbar, then select the **Stoichiometry** page.

- 2 Set species **Aa** and **Ba** as the slave species by selecting the corresponding check boxes in the **Slave** column. Clear the other species' check boxes.
- 3 Click **Close**.

The selection of slave species is automatic in Reaction Engineering Lab. In the present model you modify this choice and set the concentrations of adsorbed proteins as slave species. This is appropriate, as surface concentrations are difficult to evaluate experimentally. In general, it is good practice to review the default slave species selections in models containing equilibrium reactions.

COMPUTING THE SOLUTION

Start by investigating the kinetics in a perfectly mixed system in the Reaction Engineering Lab. To reproduce results of Figure 4-72, follow the steps listed below.

- 1 Choose **Simulation>Solver Parameters**.
- 2 In the **Times** edit field, type 10.
- 3 Click **OK**.
- 4 Click the **Solve Problem** button (=) on the Main toolbar.

You should now see the plot reproduced in Figure 4-72 on your screen.

SPECIES INTERFACE

Continue by modifying the model for export to COMSOL Multiphysics.

- 1 Choose **Model>Reaction Settings**.
- 2 With the **Species** tab active, go to the **General** page.
- 3 Select species **A** from the **Species selection** list, type 0 in the **c_0** edit field, and clear the **Lock concentration/activity** check box.
- 4 Select species **B** from the **Species selection** list, type 0 in the **c_0** edit field, and clear the **Lock concentration/activity** check box.

In the geometric subdomain, the initial concentrations of the protein species are zero.

- 5 Click **Close**.

EXPORT SETTINGS

- 1 From the **File** menu, select **Export>Model to COMSOL Multiphysics**.
The **Start COMSOL Multiphysics** dialog box appears.
- 2 From the **Space dimension** list, select **ID**. Click **OK**.

- 3 In the dialog box that launches, go to the **Export mass balance** area and select **Diffusion: New** from the **Application mode** list.
- 4 In the **Group name** edit field, type **protein**.
- 5 Move to the **Export energy balance** area and clear the check box in the upper left corner.
- 6 Click the **Export** button at the bottom of the dialog box.

Modeling Using COMSOL Multiphysics

GEOMETRY MODELING

- 1 Hold down the Shift key and click the **Line** button on the Draw toolbar to launch the **Line** dialog box.
- 2 In the **x** edit field, type 0.1×10^{-5} , then click **OK**.
- 3 Click the **Zoom Extents** button.

PHYSICS SETTINGS

Subdomain Settings

- 1 Choose **Physics>Subdomain Settings**.
- 2 From the **Subdomain selection** list, select **1**.
- 3 From the **Group** list, select **protein**.

The Reaction Engineering Lab created this group during the export process from the Reaction Engineering Lab to COMSOL Multiphysics. Note how all the relevant edit fields are automatically filled in. On the **Stoichiometry** page you can review the selection of slave species. If you want to make any changes to this selection, go back to the Reaction Engineering Lab, make the necessary changes, and then perform a new export.

- 4 Click **OK**.

Boundary Conditions

- 1 Choose **Physics>Boundary Settings**.
- 2 For all four species, enter the following boundary conditions:

SETTINGS	BOUNDARY 1	BOUNDARY 2
Type	Concentration	Insulation/Symmetry

- 3 From the **Boundary selection** list, select **1**.

- 4 Select the tab for each of the four species, in turn, and type the corresponding value from the table below in the **Concentration** edit field:

SPECIES	CONCENTRATION
c_A	1
c_Sa	0.1
c_S	1
c_B	1

- 5 Click **OK**.

GEOMETRY MODELING

- 1 Click the **Draw Mode** button on the Main toolbar.
- 2 Shift-click the **Point** button, then in the **x** edit field type $0.5e-5$.
This step places a point in the middle of the modeling domain. This point is where the model evaluates the change in species concentrations over time.
- 3 Click **OK**.

MESH GENERATION

- 1 Choose **Mesh>Free Mesh Parameters**.
- 2 Click the **Boundary** tab, select Boundary 1, and type $1e-8$ in the **Maximum element size** edit field.
- 3 Click **OK**.

COMPUTING THE SOLUTION

- 1 Click the **Solver Parameters** button on the Main toolbar. Check in the **Solver** list that **Time dependent** is selected.
- 2 Go to the **Times** edit field and enter the vector $0:0.01:4$. Click **OK**.
- 3 Solve the problem by clicking the **Solve** button (=) on the Main toolbar.

POSTPROCESSING THE SOLUTION

The following steps reproduce Figure 4-73:

- 1 Choose **Postprocessing>Domain Plot Parameters**.
- 2 On the **General** page, select the **Keep current plot** check box.
- 3 On the **Point** page, locate the **Boundary selection** list and choose **2**.
- 4 From the **Predefined quantities** list, select **Concentration, c_Aa**.

- 5 Click the **Line Settings** button. Select the **Legend** check box. From the **Line marker** list, select **Triangle**. Click **OK**.
- 6 Click **Apply** to plot the first graph.
- 7 Still on the **Point** page, from the **Predefined quantities** list, select **Concentration, c_Ba**.
- 8 Click the **Line Settings** button. From the **Line color** list, select **Color**, and from the **Line marker** list, select **Square**. Click **OK**.
- 9 Click **Apply** to generate the second graph.
- 10 On the **Point** page, go to the **Predefined quantities** list and select **Concentration, c_Sa**.
- 11 Click the **Line Settings** button. From the **Line color** list select **Color**. Click the **Color** button, select green from the palette, and click **OK**.
- 12 From the **Line marker** list, select **Circle**, then click **OK**.
- 13 Click **OK** to add the third graph to the plot.
- 14 Click the **Edit Plot** button in the Figure window.
- 15 Locate the list on the left of the **Edit Plot** dialog box, then select **Axes**.
- 16 Go to the **Title** edit field and type Adsorbed species.
- 17 Go to the **y label** edit field and enter Concentration.
- 18 Return to the list on the left of the **Edit Plot** dialog box, and this time select the first **Line** entry.
- 19 Go to the **Legends** edit field, enter c_Aa, then select the **Show legend** check box.
- 20 In the list to the left in the **Edit Plot** dialog box select the second **Line** entry.
- 21 Go to the **Legends** edit field, enter c_Ba, then select the **Show legend** check box.
- 22 Return once more to the list in the left in the **Edit Plot** dialog box, then select the third **Line** entry.
- 23 In the **Legends** edit field enter c_Sa, then select the **Show legend** check box.
- 24 Click **OK**.

Neutralization of Chlorine in a Scrubber

Introduction

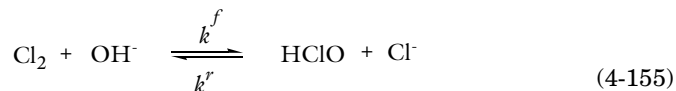
This example studies the kinetics of the neutralization of chlorine gas in water solution. It is of particular interest to investigate whether a simple two-reaction mechanism adequately describes the system, or whether a further two reactions are also required.

Such a study could well be useful for sizing a chlorine scrubber. This includes choosing the size and shape of the packing within the scrubber as well as the flow rates for the species to be cleaned and the scrubber fluid.

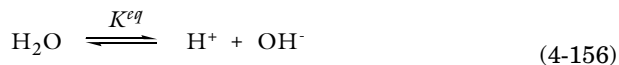
In this first study, assume that the fluid volume is perfectly mixed. This means that the chlorine has dissolved to an almost saturated state ($1 \cdot 10^{-2} \text{ mol/m}^3$) and that the hydroxide has also mixed well throughout, as would be the case for a very small amount of fluid in a scrubber. Starting from this assumption, you can investigate the time-scale of the reactions, the amount of hydroxide required to neutralize the chlorine, and the likely concentrations of the resulting products. A further criterion is that the final solution is slightly alkaline.

Model Definition

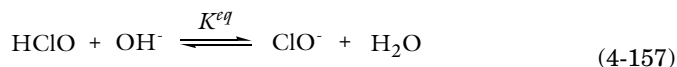
The model includes two different reaction schemes, and its solution provides an estimate of how much hydroxide should be used to neutralize the chlorine in a perfectly-mixed solution. This first instance only considers the reaction where the hydroxide ion neutralizes the chlorine:



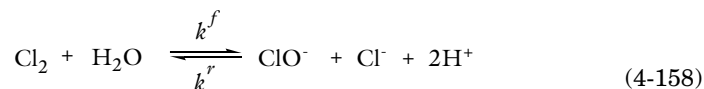
In this case, also consider the equilibrium reaction of the hydroxide ion with the hydrogen ion and water:



In a second case, you investigate the situation where the produced hypochlorous acid species can dissociate by reacting with the hydroxide ion:



Chlorine can also react directly with water to produce a hypochlorous acid and chloric acid:



Traditionally, when setting up the reaction terms and mass balances of a reaction scheme, you use a full description of the mass action law. This includes reaction rate constants for both the forward and reverse reactions in the reaction term and subsequent mass balances. In the present example, you can assume that the forward and reverse reaction rate constants for Equation 4-156 and Equation 4-157 are not available, and that you have to use equilibrium constants instead. This is easily achieved using the Reaction Engineering Lab.

You find the thermodynamic and kinetic data for the system in Ref. 1 and Ref. 2. For convenience, they are reproduced in Table 4-3 below.

TABLE 4-3: KINETIC PARAMETERS FOR THE NEUTRALIZATION REACTIONS

REACTION	k^f	k^r	K^{eq}
Equation 4-155	$1.565 \cdot 10^6$	$3.485 \cdot 10^{-5}$	
Equation 4-156			$1 \cdot 10^8$
Equation 4-157			$2.79 \cdot 10^3$
Equation 4-158	16.48	$3.7 \cdot 10^{-10}$	

Eight species result from the reactions in Equation 4-155 through Equation 4-158, of which two— H_2O and HCl —are assumed to have initial concentrations equal to unity. These conditions can easily be set in the Reaction Engineering Lab. The only other non-vanishing initial concentration is that for chlorine in water, which is set to the value of $1 \cdot 10^{-2} \text{ mol/m}^3$. Yet, it is always useful to avoid zero concentrations throughout a specified reaction model, because they often show up in the participating equations, such as in those describing equilibrium. Therefore, some arbitrary trace concentrations are entered for the other species.

CASE I

Figure 4-74 shows the concentration profile after 30 ms where only chlorine's reaction with hydroxide and the water dissociation reaction are considered.

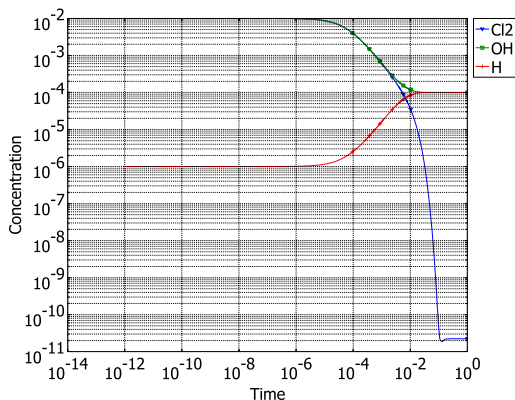


Figure 4-74: Dissolved chlorine (aq), hydrogen ion, and hydroxide ion concentration in a log scale versus logarithmic time graph. Only chlorine's reaction with hydroxide and the water dissociation reaction are considered.

Initially, the chlorine quickly decays through the ready abundance of hydroxide ions. It continues to be reduced at a slower pace through the reaction with hydroxide ions that are, in turn, being produced through the water dissociation reaction. The initial concentration of the hydroxide ions is sufficiently large to guarantee an alkaline final solution.

A basic conclusion that can be drawn from this figure, is that a contact time of at least 30 ms is required to reduce the chlorine concentration to levels below 10^{-6} mol/m³. This is quite a short time in comparison with the kinetics associated with the absorption and transport of chlorine into water.

CASE 2

Figure 4-75 shows the case where all four reactions are considered. It is apparent that the final solution is acidic, and that not enough of the chlorine is reduced.

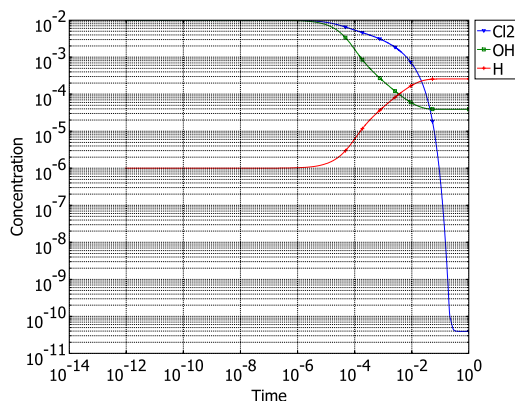


Figure 4-75: Dissolved chlorine (aq), hydrogen ion, and hydroxide ion concentration in a log scale versus logarithmic time graph. All reaction mechanism steps are considered.

Figure 4-76 shows the case where all four reactions are considered and the hydroxide concentration has been adjusted.

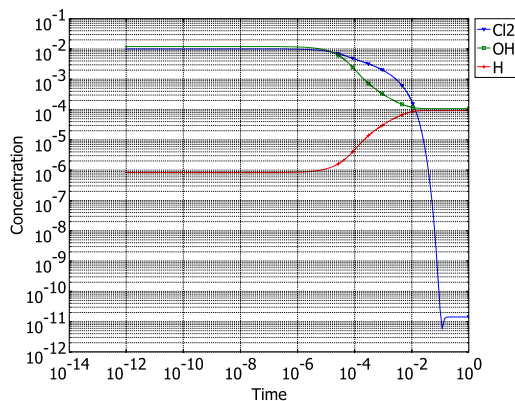


Figure 4-76: Dissolved chlorine (aq), hydrogen ion, and hydroxide ion concentration in a log scale versus time graph. All reaction mechanism steps are considered and the hydroxide concentration has been adjusted.

An interesting result from Figure 4-76 is that the chlorine concentration is an order of magnitude greater than in Figure 4-74. In this case, a contact time larger than 30 ms may be required to reduce the concentration to 10^{-6} mol/m^3 .

An overall conclusion is that the consideration of the two extra reactions in the mechanism is important, because these reactions decelerate the overall kinetics. This holds irrespective of the fact that one of the extra reactions, the one displayed in Equation 4-158, also leads to the decay of chlorine.

References

1. C. W. Spalding, *Reaction Kinetics in the Absorption of Chlorine into Aqueous Media*, AIChE J., 27, 856 (1981).
2. S. S. Ashour, E. B. Rinker, and O. C. Sandall, *Absorption of Chlorine into Aqueous Bicarbonate Solutions and Aqueous Hydroxide Solutions*, AIChE J., 42, 671 (1996).

Model Library path: Process_Chemistry/chlorine_scrubber

Modeling Using COMSOL Reaction Engineering Lab

- 1 Start the Reaction Engineering Lab.
- 2 Click **New** in the **Model Navigator**.
- 3 In the main user interface window, click the **Reaction Settings** button.

REACTIONS INTERFACE

- 1 Create four entries in the **Reaction selection** list by clicking the **New** button four times.
- 2 Enter the following reaction formulas by first selecting the appropriate row in the **Reaction selection** list and then typing the corresponding text in the **Formula** edit field.

REACTION ID #	REACTION FORMULA
1	$\text{Cl}_2 + \text{OH}^- \rightleftharpoons \text{HClO} + \text{Cl}^-$
2	$\text{H} + \text{OH} = \text{H}_2\text{O}$
3	$\text{HClO} + \text{OH}^- = \text{ClO}^- + \text{H}_2\text{O}$
4	$\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{ClO}^- + \text{HCl}$

- 3 Enter the following forward rate constants, reverse rate constants, and equilibrium constants by first selecting the appropriate row in the **Reaction selection** list and then typing the data in the appropriate edit field.

REACTION ID #	k^f	k^r	K^{eq}_0
1	1.565e6	3.485e-5	
2			1e8
3			2.79e3
4	16.48	3.7e-10	

SPECIES INTERFACE

- 1 Click the **Species** tab.
- 2 Verify that the **Species selection** list has the eight species expected from entering the reaction formulas above.
- 3 On the **General** page, enter the following initial concentrations in the c_0 edit field by selecting, one by one, the appropriate entries in the **Species selection** list.

SPECIES NAME	c_0
Cl2	1e-2
OH	1e-2
HClO	1e-11
Cl	1e-11
H	1e-6
H2O	1
ClO	1e-11
HCl	1

- 4 The concentrations of the species H₂O and HCl affect the reaction kinetics but are constant during the reaction. Impose these conditions by selecting the respective species in the **Species selection** list and then selecting the **Lock concentration/activity** check box.
- 5 Click **Close**.

REACTIONS INTERFACE—CASE I

- 1 From the **Model** menu, select **Reaction Settings**.
- 2 Click the **Reactions** tab.

- 3 Deactivate the third and fourth reactions—the hypochlorous acid dissociation and chlorine reaction with water, respectively—by clearing the check boxes next to these reactions.

- 4 Click **Close**.

OPTIONS AND SETTINGS

The following steps describe how to change the default slave species selection from OH to H.

- 1 From the **Model** menu, select **Model Settings**.
- 2 On the **Stoichiometry** page, clear the check box for OH and select the check box for H.
- 3 Click **Close**.

COMPUTING THE SOLUTION—CASE 1

- 1 Choose **Simulation>Solver Parameters**.
- 2 In the **Time stepping** area, find the **Times** edit field and type 1.
- 3 In the **Relative tolerance** edit field, type $1e-9$.
- 4 In the **Absolute tolerance** edit field, type $1e-10$.
- 5 Click **OK**.
- 6 Click the **Solve Problem** button (=) on the Main toolbar.

POSTPROCESSING AND VISUALIZATION—CASE 1

- 1 Choose **Postprocessing>Plot Parameters**.
- 2 Click the << button to clear the **Quantities to plot** list.
- 3 Go to the **Predefined quantities list** and Ctrl-click to select the entries Cl₂, OH, and H.
- 4 Click the > button to add the selected entries to the **Quantities to plot** list.
- 5 Click the **Line Settings** button.
- 6 From the **Line color** list, select **Cycle**.
- 7 From the **Line marker** list, select **Cycle** and then click **OK**.
- 8 Click **OK**.
- 9 Select the **X log** and **Y log** buttons on the Main toolbar to generate Figure 4-74.

REACTIONS INTERFACE—CASE 2

- 1 Choose **Model>Reaction Settings**.
- 2 Click the **Reactions** tab.

- 3 Reactivate the third and fourth reactions by selecting the check boxes beside these reactions.

OPTIONS AND SETTINGS

When activating or deactivating reactions, the selection of slave species is automatically changed. Therefore we need to manually alter the selection such that H and HClO become slave species.

- 1 From the **Model** menu, select **Model Settings**.
- 2 On the **Stoichiometry** page, select the check boxes for HClO and H and ensure that the check boxes for all other species are cleared.
- 3 Click **Close**.

SPECIES INTERFACE—CASE 2

- 1 Click the **Species** tab.
- 2 Select OH and type 1.2×10^{-2} in the **c₀** edit field to change the initial concentration.
- 3 Click **Close**.

COMPUTING THE SOLUTION—CASE 2

Click the **Solve Problem** button on the Main toolbar.

POSTPROCESSING AND VISUALIZATION—CASE 2

Click the **X log** and **Y log** buttons on the Main toolbar to create Figure 4-76.

To create Figure 4-75, simply change the hydroxide ion (OH) concentration back to its original value of 1×10^{-2} and re-solve the model.

Non-Isothermal Plug-Flow Reactor

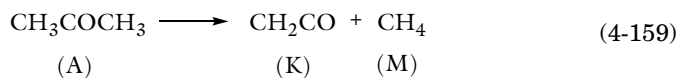
Introduction

This model considers the thermal cracking of acetone, which is a key step in the production of acetic anhydride. The gas phase reaction takes place under non-isothermal conditions in a plug-flow reactor. As the cracking chemistry is endothermic, control over the temperature in the reactor is essential in order to achieve reasonable conversion. When the reactor is run under adiabatic conditions, the model shows how the conversion of acetone can be affected by mixing the reactant with inert. Furthermore, it is illustrated how to affect the conversion of acetone by means of a heat exchanger supplying energy to the system.

The example details the use of the predefined Plug-flow reactor type in the Reaction Engineering Lab and how to set up and solve models describing non-isothermal reactor conditions. You will learn how to model adiabatic reactor conditions as well as how to introduce heat exchange.

Model Definition

This model is related to an example found in Ref. 1. An essential step of in the gas-phase production of acetic anhydride is the cracking of acetone (*A*) into ketene (*K*) and methane (*M*):



The rate of reaction is

$$r_1 = k_1 c_A \quad (4-160)$$

where the rate constant is given by the Arrhenius expression

$$k_1 = A_1 \exp\left(-\frac{E_1}{R_g T}\right) \quad (4-161)$$

For the decomposition of acetone described above, the frequency factor is $A_1 = 8.2 \cdot 10^{14}$ (1/s), and the activation energy is $E_1 = 284.5$ (kJ/mol).

Chemical reaction takes place under non-isothermal conditions in a plug-flow reactor, illustrated schematically in Figure 4-77.

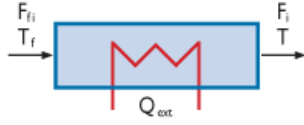


Figure 4-77: The Plug-flow reactor is a predefined reactor type in the Reaction Engineering Lab.

Species mass balances are described by:

$$\frac{dF_i}{dV} = R_i \quad (4-162)$$

where F_i is the species molar flow rate (mol/s), V is the reactor volume (m^3), and R_i is the species rate expression ($\text{mol}/(\text{m}^3 \cdot \text{s})$). Concentrations needed to evaluate rate expressions are found from:

$$c_i = \frac{F_i}{v} \quad (4-163)$$

where v is the volumetric flow rate (m^3/s). By default, the Reaction Engineering Lab treats gas phase reacting mixtures as being ideal. Under this assumption the volumetric flow rate is given by:

$$v = \frac{p}{R_g T} \sum_i F_i \quad (4-164)$$

where p is the pressure (Pa), R_g denotes the ideal gas constant ($8.314 \text{ J}/(\text{mol} \cdot \text{K})$), and T is the temperature (K).

The reactor energy balance is given by:

$$\sum_i F_i C_{p,i} \frac{dT}{dV} = w_s + Q + Q_{\text{ext}} \quad (4-165)$$

In Equation 4-165, $C_{p,i}$ represents the species molar heat capacity ($\text{J}/(\text{mol} \cdot \text{K})$), w_s is the shaft work per volume ($\text{J}/(\text{m}^3 \cdot \text{s})$). Q denotes the heat due to chemical reaction ($\text{J}/(\text{m}^3 \cdot \text{s})$):

$$Q = -\sum_j H_j r_j \quad (4-166)$$

where H_j is the heat produced by reaction j . The term Q_{ext} represents external heat added or removed from the reactor. The present model treats both adiabatic reactor conditions:

$$Q_{\text{ext}} = 0$$

and the situation where the reactor is equipped with a heat exchanger jacket. In the latter case Q_{ext} is given by:

$$Q_{\text{ext}} = Ua(T_{\text{amb}} - T) \quad (4-167)$$

where U is the overall heat transfer coefficient ($\text{J}/(\text{m}^2 \cdot \text{s} \cdot \text{K})$), a is the effective heat transfer area per unit of reactor volume ($1/\text{m}$), and T_{amb} is the temperature of the heat exchanger medium (K). The Reaction Engineering Lab automatically sets up and solves Equation 4-162 and Equation 4-165 as the predefined Plug-flow reactor type is selected. As input to the balance equations you need to supply the chemical reaction formula, the Arrhenius parameters, the species thermodynamic properties, as well as the inlet molar feed of reactants.

Following the step-by-step instructions below, you will first model the cracking of acetone in an adiabatic plug-flow reactor. See how the acetone conversion varies with the ratio of reactant to inert in the inlet stream. In second model, add the effects of a heat exchanger jacket and observe how the added energy drives the reaction to completion.

Working with Thermodynamic Polynomials

Reaction Engineering Lab uses the following set of polynomials as default expressions describing species thermodynamic properties:

$$C_{p,i} = R_g(a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4) \quad (4-168)$$

$$h_i = R_g\left(a_1 T + \frac{a_2}{2} T^2 + \frac{a_3}{3} T^3 + \frac{a_4}{4} T^4 + \frac{a_5}{5} T^5 + a_6\right) \quad (4-169)$$

$$s_i = R_g\left(a_1 \ln T + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7\right) \quad (4-170)$$

Here, $C_{p,i}$ denotes the species' heat capacity (J/(mol·K)), T the temperature (K), and R_g the ideal gas constant, 8.314 (J/(mol·K)). Further, h_i is the species' molar enthalpy (J/mol), and s_i represents its molar entropy (J/(mol·K)). A set of seven coefficients per species are taken as input for the polynomials above. The coefficients a_1 through a_5 relate to the species heat capacity, the coefficient a_6 is associated with the species enthalpy of formation (at 0 K), and the coefficient a_7 comes from the species entropy of formation (at 0 K).

The format outlined by Equation 4-168 through Equation 4-170 is referred to as CHEMKIN or NASA format (Ref. 2). This is a well established format, and database resources list the needed coefficients for different temperature intervals. Many web based data resources exist for CHEMKIN thermodynamic data and otherwise (Ref. 3). It is therefore often a straight forward task to assemble the thermodynamic data required and then import it into your reaction model.

CREATING A THERMODYNAMIC DATA FILE

CHEMKIN thermodynamic files typically contains blocks of data, one block for each species. Such a data block is illustrated in Figure 4-78 for gas phase acetone.

```
CH3COCH3_ACETONE 110203H 6C 3O 1 OG 300.000 4000.000 1000.00 0 1
0.42619220E+01 0.23919538E-01-0.10714477E-04 0.22496890E-08-0.18079303E-12 2
-0.27708340E+05 0.37906279E+01 0.15848079E+01 0.27413605E-01-0.91426603E-05 3
-0.66768869E-09 0.34781512E-12-0.26678575E+05 0.18843809E+02 4
```

Figure 4-78: Thermodynamic data block on the CHEMKIN format.

The first line starts with the species label, given with a maximum of 18 characters, followed by a 6 character comment space. Then follows a listing of the type and number of atoms that constitute the species. The G comments that this is gas phase data. The line ends with listing of three temperatures, defining two temperature intervals. Lines 2 through 4 contain two sets of the polynomial coefficients, a_1 through a_7 . The first set of coefficients is valid for the upper temperature interval, and the second for the lower interval.

A complete CHEMKIN thermodynamics file has the structure illustrated in Figure 4-79.

```
thermo
  300.000 1000.000 4000.000
A      110203H  6C  3O  1  OG  300.000 4000.000 1000.00  0 1
  0.42619220E+01 0.23919538E-01-0.10714477E-04 0.22496890E-08-0.18079303E-12  2
-0.27708340E+05 0.37906279E+01 0.15848079E+01 0.27413605E-01-0.91426603E-05  3
-0.66768869E-09 0.34781512E-12-0.26678575E+05 0.18843809E+02  4
K      110203H  2C  2O  1  OG  300.000 4000.000 1000.00  0 1
  0.47307523E+01 0.84849084E-02-0.37289848E-05 0.77166210E-09-0.61322345E-13  2
-0.76492303E+04-0.68485049E+00 0.15410946E+01 0.21513643E-01-0.25750130E-04  3
  0.18486377E-07-0.55939702E-11-0.69557078E+04 0.14808619E+02  4
M      110203H  4C  1  0  OG  300.000 4000.000 1000.00  0 1
  0.47238333E+00 0.12680758E-01-0.55093741E-05 0.11295575E-08-0.89103779E-13  2
-0.96424500E+04 0.16199090E+02 0.38717898E+01-0.42480466E-02 0.24540181E-04  3
-0.21780766E-07 0.63010622E-11-0.10144425E+05 0.66008135E+00  4
N2     110203N  2  0  0  OG  300.000 4000.000 1000.00  0 1
  0.27292633E+01 0.17776002E-02-0.76185598E-06 0.15386678E-09-0.11961307E-13  2
-0.83679340E+03 0.70662127E+01 0.36962069E+01-0.12983164E-02 0.24640713E-05  3
-0.93801238E-09-0.37036420E-13-0.10631030E+04 0.22199845E+01  4
end
```

Figure 4-79: Thermodynamic data file on the CHEMKIN format.

The keyword **thermo** always starts the text file. The subsequent line lists three temperatures, defining two temperature intervals. These intervals are used if no intervals are provided in the species specific data. Then follows the species data blocks, in any order. The keyword **end** is the last entry in the file.

The data file reproduced in Figure 4-79 is used in the present model. It was constructed by creating a text-file with species data blocks from the Sandia National Labs Thermodynamics resource (Ref. 4).

USING SUBSETS OF THERMODYNAMIC COEFFICIENTS

In some instances, not all coefficients a_1 through a_7 are available. Coefficients may also be on a format differing from the NASA or CHEMKIN style. Input parameters can still be put on the form of Equation 4-168 to Equation 4-170, as illustrated below.

For species A, K, M, and N2, Ref. 1 lists polynomials for the heat capacity on the form:

$$C_{p,i} = a_1' + a_2'T + a_3'T^2 \quad (4-171)$$

Furthermore, the species enthalpies of formation at $T_{\text{ref}} = 298$ K are provided:

SPECIES	a_1'	a_2'	a_3'	$h(298)$
A	26.63	0.183	-45.86e-6	-216.67e3
K	20.04	0.0945	-30.95e-6	-61.09e3

SPECIES	a_1'	a_2'	a_3'	$h(298)$
M	13.39	0.077	-18.71e-6	-71.84e3
N2	6.25	8.78e-3	-2.1e-8	0

The data in the table above can be correlated with the polynomials given by Equation 4-168 and Equation 4-169 by noting the relations:

$$a_n = \frac{a_n'}{R_g} \quad n = 1, \dots, 5 \quad (4-172)$$

$$a_6 = \frac{h(T_{\text{ref}})}{R_g} - \left(a_1 T_{\text{ref}} + \frac{a_2}{2} T_{\text{ref}}^2 + \frac{a_3}{3} T_{\text{ref}}^3 \right) \quad (4-173)$$

Using Equation 4-172 and Equation 4-173, you find the coefficients to enter in the Reaction Engineering Lab GUI.

SPECIES	a_1	a_2	a_3	a_6
A	3.20	2.20e-2	-5.52e-6	-2.79e4
K	2.41	1.14e-2	-3.72e-6	-8.54e3
M	1.61	9.26e-3	-2.25e-6	-9.87e3
N2	0.752	1.06e-3	-2.53e-9	-2.71e2

Read more about how to work with thermodynamic data in the section “Working with Predefined Expressions” on page 90.

Results

In a first model, the plug-flow reactor is run under adiabatic conditions. The reactor is fed with a total molar flow of 38.3 mol/s. The inlet stream consists of a mixture of reactant acetone and inert nitrogen, as specified by:

$$F_A = 38.3A_{\text{frac}}$$

$$F_{N2} = 38.3(1 - A_{\text{frac}})$$

Figure 4-80 shows the reactor temperature as a function of the reactor volume for the mixing conditions, $A_{\text{frac}} = 1, 0.5, 0.1$, and 0.01. As the cracking of acetone is

endothermic, the reactor temperature decreases along the reactor length; the effect being more pronounced as the fraction acetone increases.

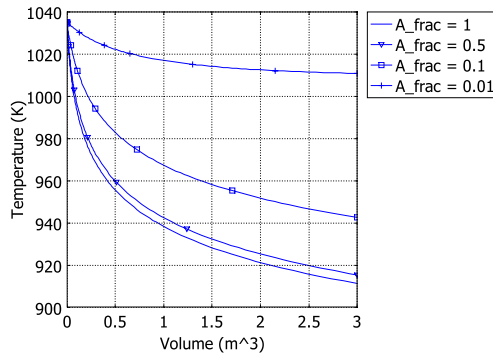


Figure 4-80: The reactor temperature (K) as a function of reactor volume (m^3), plotted for a number of feed conditions.

Figure 4-81 shows the conversion of acetone for the different mixing conditions. Conversion increases although the concentration of acetone decreases, due to the temperature effects. When pure acetone ($A_{frac} = 1$) enters the reactor conversion is no more than 24% at the reactor outlet.

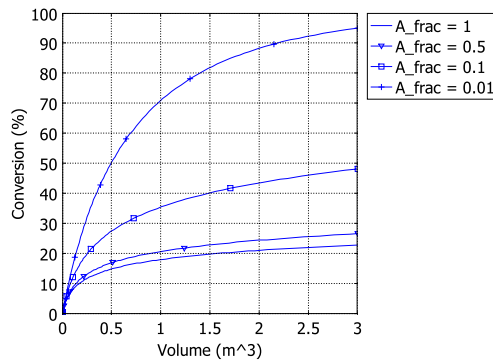


Figure 4-81: The conversion of acetone (%) as a function of reactor volume (m^3), plotted for a number of feed conditions.

Figure 4-82 shows the reaction rates as a function of reactor volume. Note that under the simulated conditions reaction rates decrease as conversion increases, thereby affecting the net production rate of ketene and methane.

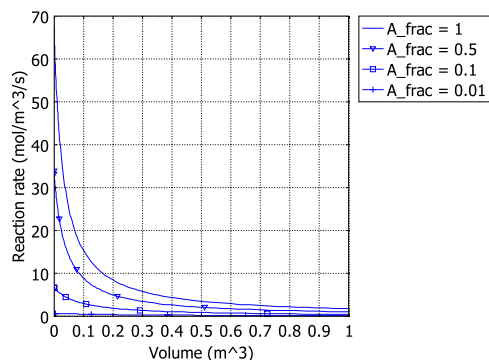


Figure 4-82: The rate of the acetone cracking reaction (mol/(m³·s)) as a function of reactor volume (m³), plotted for a number of feed conditions.

Figure 4-83 shows the temperature profile of the plug-flow reactor ($A_{\text{frac}} = 1$) as a heat exchanger supplies energy to the reacting system. Initially the energy consumption of the cracking reaction is dominant, and the temperature in the system drops. As the reaction rate drops off, the heat exchanger starts to heat up the system. The heating rate decreases with the temperature difference between the heat exchanger medium and reacting fluid.

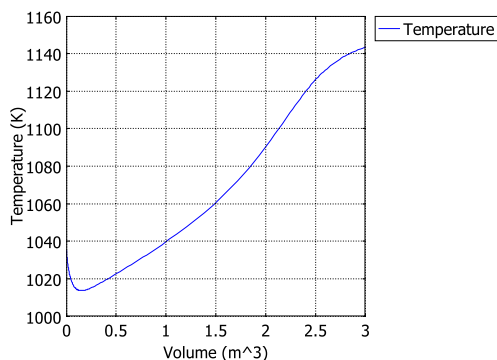


Figure 4-83: Temperature (K) as a function of volume (m³), for a reactor equipped with a heat exchanger jacket.

Figure 4-84 shows the conversion of acetone along with the reaction rate ($A_{\text{frac}} = 1$). Comparing with Figure 4-81 and Figure 4-82, note how the heat exchanger allows for relatively high reaction rates while maintaining high conversion.

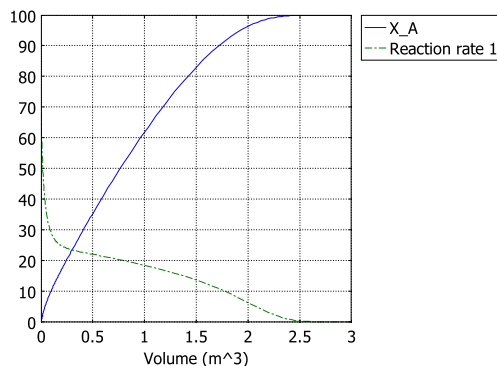


Figure 4-84: The conversion of acetone (%) and reaction rate ($\text{mol}/(\text{m}^3 \cdot \text{s})$) as a function of reactor volume (m^3).

References

1. H.S. Fogler, *Elements of Chemical Reaction Engineering 3rd Ed.*, Prentice Hall PTR, 1999, example 8-7, pp. 462–468.
2. S. Gordon and B.J. McBride, *Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouquet Detonations*, NASA-SP-273, 1971.
3. See e.g. <http://www.comsol.com/reaction>
4. <http://www.ca.sandia.gov/HiTempThermo/index.html>

Model Library path: Process_Chemistry/nonisothermal_plugflow

Modeling Using COMSOL Reaction Engineering Lab

MODEL NAVIGATOR

- I Start the Reaction Engineering Lab.

- 2 In the **Model Navigator**, click the **New** button to launch the main user interface.

OPTIONS AND SETTINGS

- 1 Click the **Model Settings** button on the Main toolbar.
- 2 Select **Plug-flow** from the **Reactor type** list.
- 3 Select the **Calculate thermodynamic properties** check box.
- 4 Select the **Include energy balance** check box.
- 5 On the **General** page, type 162e3 in the **p** edit field.
- 6 Click the **Init** page, and type 1035 in the **T(V₀)** edit field.
- 7 Click **Close**.

Now, define a number of constants that will be used later.

- 1 Select the menu item **Model>Constants**, then enter the following data:

NAME	EXPRESSION
Ua	16500
T_amb	1150
A_frac	1

- 2 Click **OK**.
- 3 Select the menu item **Model>Expressions**, then enter the following data:

NAME	EXPRESSION
X_A	(F0_A-F_A)/F0_A*100

- 4 Click **OK**.

REACTIONS INTERFACE

- 1 From the **Model** menu, select **Reaction Settings**.
- 2 Create a new entry in the **Reaction selection** list by clicking the **New** button.
- 3 Type A=>K+M in the **Formula** edit field.
- 4 Select the **Use Arrhenius expressions** check box.
- 5 Type 8.2e14 in the **A** edit field.
- 6 Type 284.5e3 in the **E** edit field.

SPECIES INTERFACE

- 1 While still in the **Reaction Settings** dialog box, click the **Species** tab.

- 2 Verify that the **Species selection** list has the three species (A, K, and M).
- 3 Click the **New** button and type N2 in the **Formula** edit field. This adds the inert species N2 to the reacting flow.
- 4 Click the **Feed Stream** page.
Note that for a plug-flow reactor you need to specify the inlet molar flows (F_0), in contrast to the batch reactor types, where you need to provide the initial species concentrations (c_0).
- 5 Select species A from the **Species selection** list and enter $38.3 \cdot A_frac$ in the **F₀** edit field.
- 6 Select species N2 from the **Species selection** list and enter $38.3 \cdot (1 - A_frac)$ in the **F₀** edit field. You will use the parameter A_frac to vary the mix of reactant and inert, for a constant molar flow at the inlet
- 7 Click **Close**.

IMPORT THERMODYNAMIC DATA

Proceed to import the thermodynamics data file.

- 1 Select **File>Import>CHEMKIN Thermo Input File**.
- 2 Browse to the file `nonisothermal_plugflow_thermo.txt` and click the **Import** button.

You can inspect the loaded data in the **Reaction Settings** dialog box. Go to the **Species>Thermo** page and click the **Polynomial coefficients** edit field. Here you will find the thermodynamic coefficients a_1 through a_7 for each species.

COMPUTING THE SOLUTION

- 1 Open the **Simulation>Solver Parameters** dialog box.
- 2 Type 3 in the **Reactor volumes** edit field.
- 3 Clear the **Stop If Steady State is reached first** check box.
- 4 Click **OK**.
- 5 Click the **Solve Problem** button (=) on the Main toolbar.

POSTPROCESSING AND VISUALIZATION

The default plot shows the molar flows of the participating species as a function of the reactor volume. To create Figure 4-80, follow these steps:

- 1 Choose **Postprocessing>Plot Parameters** (or click the corresponding button on the Main toolbar).

- 2 Click the << button to remove all entries from the **Quantities to plot** list.
- 3 Select **Temperature** from the **Predefined quantities** list and click the **Add** button, >.
- 4 Select **New Figure** in the **Plot in** list.
- 5 Select the **Keep current plot** check box.
- 6 Click **Apply**.
- 7 Select **Model>Constants**.
- 8 Change the **A_frac** entry to 0.5, then click **Apply**.
- 9 Click the = button on the Main toolbar.
- 10 Repeat Steps 8 and 9 for the **A_frac** values 0.1 and 0.01.
- 11 Click the **Figure 1** window.
- 12 Click the **Edit Plot** button.
- 13 Select the first **Line** entry, type $A_frac = 1$ in the **Legends** edit field.
- 14 Select the second **Line** entry, type $A_frac = 0.5$ in the **Legends** edit field, and choose **Triangle** from the **Line marker** list.
- 15 Select the third **Line** entry, type $A_frac = 0.1$ in the **Legends** edit field, and choose **Square** from the **Line marker** list.
- 16 Select the fourth **Line** entry, type $A_frac = 0.01$ in the **Legends** edit field, and choose **Plus sign** from the **Line marker** list.
- 17 Click **OK** to close the **Edit Plot** dialog.
- 18 Click **OK** to close the **Constants** dialog.

Create Figure 4-81 and Figure 4-82 in the same fashion as just described, adding **X_A** and then **Reaction rate 1** to the **Quantities to plot** list, found in the **Plot Parameters** dialog.

- 1 In the **Plot Parameters** dialog box, clear the **Keep current plot** check box.
- 2 Select **Main axes** from the **Plot in** list.
- 3 Click **OK**.

Move on to see how conversion is affected as a heat exchanger jacket supplies heat to the reacting mixture.

OPTIONS AND SETTINGS

- 1 Select the menu item **Model>Model Settings**.
- 2 Click the **Energy Balance** tab.

- 3 Type $U_a \cdot (T_{\text{amb}} - T)$ in the **Q_{ext}** edit field.
- 4 Click **Close**.
- 5 Select the menu item **Model>Constants**.
- 6 Change the value **A_frac** entry to 1, then click **OK**.

COMPUTING THE SOLUTION

Click the **Solve Problem** button (\Rightarrow) on the Main toolbar.

POSTPROCESSING AND VISUALIZATION

To create Figure 4-83, follow these steps:

- 1 Choose **Postprocessing>Plot Parameters** (or click the corresponding button on the Main toolbar).
- 2 Click the **<<** button to remove all entries from the **Quantities to plot** list.
- 3 Select **Temperature** from the **Predefined quantities** list and click the **Add** button, **>**.
- 4 Click **Apply**.

To create Figure 4-84, follow steps below:

- 1 Click the **<<** button to remove all entries from the **Quantities to plot** list.
- 2 Select **X_A** from the **Predefined quantities** list and click the **Add** button, **>**.
- 3 Select **Reaction rate I** from the **Predefined quantities** list and click the **Add** button, **>**.
- 4 Click **OK**.

Polymerization in a Semibatch Reactor

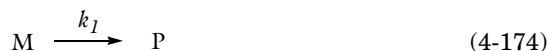
Introduction

As reactant monomer converts into polymer chains, the density of the reacting mixture often changes notably. In this example you will look at how this effect impacts the total production of polymer in a process. The liquid phase polymerization takes place in a semibatch reactor, where two operating conditions are compared. In the first scenario, the feed of monomer to the reactor is turned off once the maximum volume capacity is reached. In a second scenario, the feed of monomer is allowed to continuously compensate for the volume change due to chemical reaction.

The model illustrates the use of the Semibatch reactor type, that is predefined in the Reaction Engineering Lab. It is also shown how to set timed events, in this case, controlling the reactant feed to the reactor.

Model Definition

This model reproduces results found in Ref. 1. A liquid phase polymerization can be modeled as a first order irreversible reaction:



$$r_1 = k_1 c_M \quad (4-175)$$

In the above equations, M denotes the monomer, P the polymer, r is the reaction rate ($\text{mol}/(\text{m}^3 \text{ s})$), k is the rate constant ($1/\text{s}$), and c_M is the concentration of monomer (mol/m^3).

The polymerization takes place in a semibatch reactor with a volume capacity of 20 m^3 . Initially the reactor is charged with 10 m^3 of solvent. Pure monomer enters the reactor with a volumetric flow rate of $v_f = 1 \text{ m}^3/\text{min}$.

Figure 4-85 shows a schematic representation of the semibatch reactor.

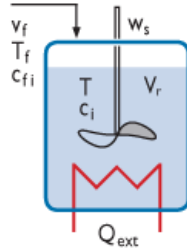


Figure 4-85: The Semibatch reactor is a predefined reactor type in the Reaction Engineering Lab.

The following mass balance describes the semibatch reactor:

$$\frac{d(c_i V_r)}{dt} = v_{f,i} c_{f,i} + R_i V_r \quad (4-176)$$

In Equation 4-176, c_i is species molar concentration (mol/m^3), $c_{f,i}$ is the species concentration (mol/m^3) of the associated feed stream $v_{f,i}$ (m^3/s), and R_i denotes the species rate expression ($\text{mol}/(\text{m}^3 \cdot \text{s})$). V_r labels the reactor volume (m^3) and is a function of time. For ideal mixtures:

$$\frac{dV_r}{dt} = \sum v_{f,i} + v_p \quad (4-177)$$

where v_p is the volumetric production rate due to chemical reaction:

$$v_p = \sum_j \sum_i v_{ij} \frac{M_i}{\rho_i} r_j V_r \quad (4-178)$$

In Equation 4-178, v_{ij} is the stoichiometric coefficient of species i in reaction j , M_i denotes the species molecular weight (kg/mol), ρ_i is the species density (kg/m^3), and r_j is the reaction rate ($\text{mol}/(\text{m}^3 \cdot \text{s})$) of reaction j .

Note that Reaction Engineering Lab automatically sets up and solves Equation 4-176 and Equation 4-177 once the Semibatch reactor type has been selected.

In the present example, the density of the monomer is $800 \text{ kg}/\text{m}^3$ and the density of the polymer $1100 \text{ kg}/\text{m}^3$. Hence, as polymer is being formed, the volume of the

reacting mixture will decrease (v_p is negative). The model investigates two operating conditions:

- *Operating Condition 1*—The monomer feed ($1 \text{ m}^3/\text{min}$) is shut off once the reactor volume reaches 20 m^3 , which occurs after 11.2 minutes. The reaction is then allowed to go to completion.
- *Operating Condition 2*—The monomer feed is adjusted to keep the reactor filled while the reaction goes to completion. This is accomplished by setting the volumetric feed equal to $-v_p$, for $t > 11.2$ minutes.

Results

Figure 4-86 shows the reactor volume as function of the run time, illustrating the two operating conditions listed above.

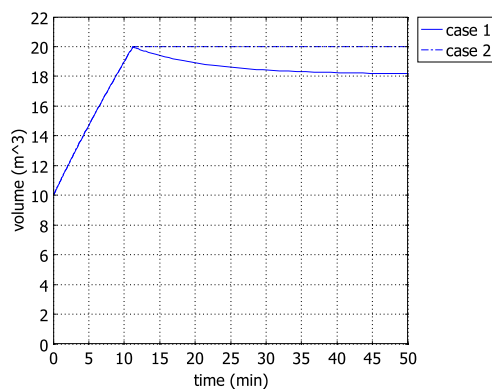


Figure 4-86: The reactor volume (m^3) as function of time (minutes) for operating condition 1 (solid line) and 2 (dash-dotted line).

Figure 4-87 illustrates the volumetric flow rate of the feed stream, v_f .

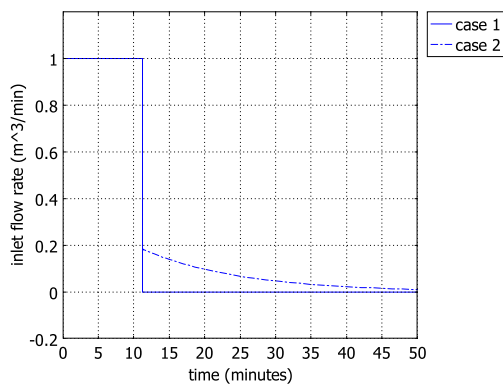


Figure 4-87: The volumetric flow rate of the feed stream (m^3/s) as function of time (minutes) for operating condition 1 (solid line) and 2 (dash-dotted line).

Figure 4-88 shows the total mass of monomer in the reactor, m_M (kg), as evaluated by the expression:

$$m_M = c_M V_r M_M$$

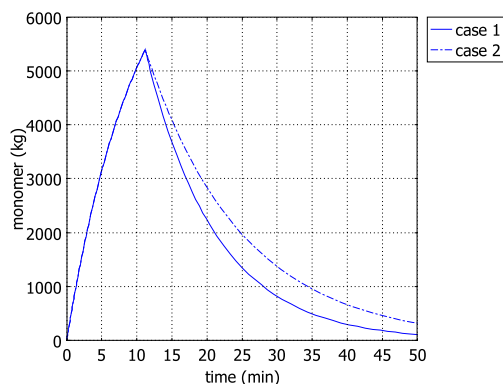


Figure 4-88: The total monomer mass in the reactor volume (kg) as function of time (minutes) for operating condition 1 (solid line) and 2 (dash-dotted line).

It is straight forward to compare the amount of produced polymer as a result of the different operating conditions. For both cases the reaction has run to completion after

approximately 3 hours. At this time, the total volume of the reacting mixture is 18.1 m³ for operating condition 1 and 20 m³ for operating condition 2. The reactor was initially charged with 10 m³ of solvent. Hence, the total mass of polymer produced is:

$$m_P = (V_{r0} - V_r)\rho_M$$

The relative increase in polymer production using operating condition 2 compared to condition 1 is then:

$$\frac{m_{P,2} - m_{P,1}}{m_{P,1}} = \frac{10 - 8.1}{8.1} = 23\%$$

Reference

1. J.B. Rawlings and J.G. Ekerdt, *Chemical Reactor Analysis and Design Fundamentals*, Nob Hill Publishing, 2004, example 4.3, pp. 139–144.

Model Library path: Process_Chemistry/semibatch_polymerization

Modeling Using COMSOL Reaction Engineering Lab

MODEL NAVIGATOR

- 1 Start the Reaction Engineering Lab.
- 2 In the **Model Navigator**, click the **New** button to launch the main user interface.

OPTIONS AND SETTINGS

- 1 Click the **Model Settings** button on the Main toolbar.
- 2 Select **Semibatch** from the **Reactor type** list.
- 3 Select **Liquid** from the **Reacting fluid** list.
- 4 Click the **Feed Streams** tab.
- 5 Click the **New** button to create **Inlet1**.
- 6 Select **Inlet1** from the **Feed stream** list, and type $1/60 * (t < 672)$ in the **v_f** edit field.
In this first model, the feed stream is turned off after 672 seconds (11.2 minutes).
- 7 Go to the **Init** page, and type 10 in the **V_r(t₀)** edit field.

- 8 Click **Close**.

REACTIONS INTERFACE

- 1 From the **Model** menu, select **Reaction Settings**.
- 2 Create a new entry in the **Reaction selection** list by clicking the **New** button.
- 3 Type $M \Rightarrow P$ in the **Formula** edit field.
- 4 Type $1/600$ in the k_f edit field.

SPECIES INTERFACE

- 1 While still in the **Reaction Settings** dialog box, click the **Species** tab.
- 2 Select the indicated entry in the **Species selection** list and enter the following properties:

SPECIES NAME	M	ρ
M	0.1	800
P	0.1	1100

There is no initial concentration of neither M nor P in the reactor volume, so the c_0 edit field retains its default value of zero for both species.

- 3 Click the **Feed Stream** page.
- 4 Select species M from the **Species selection** list select **Inlet1** from the **Name** list.
- 5 Type ρ_{M/M_M} in the c_f edit field.

As P does not enter the reactor through an inlet, there is no need to associate a feed stream with this species.

- 6 Click **Close**.

COMPUTING THE SOLUTION

- 1 Open the **Simulation>Solver Parameters** dialog box.
- 2 Type 3000 in the **Times** edit field.
- 3 Clear the **Stop if steady-state is reached first** check box.
- 4 Click **OK**.
- 5 Click the **Solve Problem** button (=) on the Main toolbar.

POSTPROCESSING AND VISUALIZATION

The default plot shows the molar concentrations of the participating species as a function of time (s). To create Figure 4-86, follow these steps:

- 1 Choose **Postprocessing>Plot Parameters** (or click the corresponding button on the Main toolbar).
- 2 Click the << button to remove all entries from the **Quantities to plot** list.
- 3 Type V_r in the **Expression** edit field and click the Add button >, to move the expression to the **Quantities to plot** list.
- 4 Go to the **x-axis data area**, select the **Expression** radio button, and click the **Expression** button.
- 5 Type $t/60$ in the **Expression** edit field and then click **OK**. This way you scale the time axis to show minutes rather than seconds.
- 6 Select **New Figure** in the **Plot in** list.
- 7 Select the **Keep current plot** check box.
- 8 Click **Apply**.

Now, run the model once again, with the volumetric flow of the feed stream adjusted so that the entire reactor volume is put to use. To accomplish this, compensate for the volume loss due to chemical reaction, as illustrated below.

- 9 Click the **Model Settings** button on the Main toolbar.
- 10 Go to the **Feed Streams** page.
- 11 Select **Inlet1** from the **Feed stream** list, and type $1/60 * (t < 672) - v_p * (t \geq 672)$ in the v_f edit field.

Now the feed stream continuously fills the reactor. Up to 672 s (11.2 min) the reactor is filled with the volumetric feed rate of $1/60$ (m^3/s), where after the feed is adjusted to exactly compensate for the volume loss due to chemical reaction, that is v_p (m^3/s). As the volume decreases with reaction, v_p is negative.

- 12 Click **Close**.
- 13 Press the = button on the Main toolbar.
- 14 Click the **Figure 1** window.
- 15 Click the **Edit Plot** button.
- 16 Select the first **Line** entry, type case 1 in the **Legends** edit field.
- 17 Select the second **Line** entry, type case 2 in the **Legends** edit field, and choose **Dash-dot line** from the **Line style** list.
- 18 Select **Axes** in the list to the left.
- 19 Clear the **y limits Auto** check box and type 0 and 22 in the first and second edit field.
- 20 Type time (min) in the **x label** edit field.

21 Type `volume (m^3)` in the **y label** edit field.

22 Click **OK** to close the **Edit Plot** dialog.

23 Click **OK** to close the **Constants** dialog.

Create Figure 4-87 and Figure 4-88 in the same fashion as just described, adding `vf_Inlet1*60` and then the expression `c_M*M_M*Vr` to the **Quantities to plot** list, found in the **Plot Parameters** dialog.

Startup of a CSTR

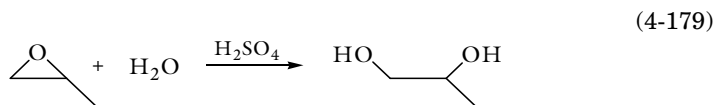
Introduction

The hydrolysis of propylene oxide into propylene glycol is an important chemical process with 400,000 metric tons produced worldwide each year. Propylene glycol finds wide application as a moisturizer in foods, pharmaceuticals, and cosmetics.

In this example you model the startup phase of a continuous stirred tank reactor (CSTR) used to produce propylene glycol. The non-isothermal process is described by a set of coupled mass and energy balances that you easily set up and solve in the Reaction Engineering Lab. The model highlights the use of the predefined CSTR reactor type and also shows how to enter the thermodynamic data needed for energy balances.

Model Description

This model reproduces the results found in Ref. 1. Propylene glycol (PrOH) is produced from the reaction of propylene oxide (PrO) with water (W) in the presence of an acid catalyst:



The reaction rate ($\text{mol}/(\text{m}^3 \cdot \text{s})$) is first order with respect to propylene oxide:

$$r_1 = -k_1 c_{PrO} \quad (4-180)$$

where the rate constant is temperature dependent according to the expression

$$k_1 = A_1 \exp\left(-\frac{E_1}{RgT}\right) \quad (4-181)$$

The Arrhenius parameters in Equation 4-181 are $A_1 = 4.71 \cdot 10^9$ (1/s) and $E_1 = 75358$ (J/mol).

The liquid phase reaction takes place in a continuous stirred tank reactor (CSTR) equipped with a heat-exchanger. Methanol (MeOH) is added to the mixture but does not react. It is further assumed that the mixture density is constant over time.

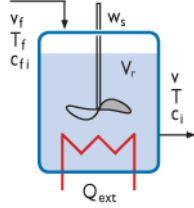


Figure 4-89: A perfectly mixed CSTR for the production of propylene glycol. The CSTR is a predefined reactor type in the Reaction Engineering Lab.

The time evolution of the non-isothermal reacting system is given by several coupled balance equations.

The species mass balances are

$$\frac{d(c_i V_r)}{dt} = v_{f,i} c_{f,i} - v c_i + R_i V_r \quad (4-182)$$

In Equation 4-182, c_i is the species molar concentration (mol/m^3), V_r denotes the reactor volume (m^3), R_i is the species rate expression ($\text{mol}/(\text{m}^3 \cdot \text{s})$), and v is the volumetric flow rate (m^3/s).

For an incompressible and ideally mixed reacting liquid, the energy balance is

$$V_r \sum_i c_i C_{p,i} \frac{dT}{dt} = Q + Q_{\text{ext}} + \sum_i v_{f,i} c_{f,i} (h_{f,i} - h_i) \quad (4-183)$$

where $C_{p,i}$ is the species molar heat capacity ($\text{J}/(\text{mol} \cdot \text{K})$), and T is the temperature (K). On the right-hand side, Q represents the heat due to chemical reaction (J/s), and Q_{ext} denotes heat added to the system (J/s), for instance by a heat exchanger. The last term signifies heat added as species flow through the reactor. In this term, h_i is the species molar enthalpy (J/mol).

This example assumes that the species heat capacities, $C_{p,i}$, represent an average over the temperature interval. The associated species' enthalpies are then given by

$$h_i = C_{p,i} (T - T_{\text{ref}}) + h_i(T_{\text{ref}}) \quad (4-184)$$

where $h_i(T_{\text{ref}})$ is the standard heat of formation at the reference temperature T_{ref} .

The heat of reaction is given by

$$Q = -V_r \sum_j H_j r_j \quad (4-185)$$

where H_j is the enthalpy of reaction (J/mol), and r_j denotes the reaction rate (mol/(m³·s)).

The heat added by the heat exchanger is given by

$$Q_{\text{ext}} = F_x C_{p,x} (T_x - T) \cdot \left[1 - \exp\left(\frac{UA}{F_x C_{p,x}}\right) \right] \quad (4-186)$$

where F is the molar flow rate (mol/s), U is the overall heat transfer coefficient (J/(K·m²·s)), and A represents the heat exchange area (m²). The subscript x refers to the heat exchanger medium, which in this case is water. T_x is the inlet temperature of the heat exchanger medium.

The following table summarizes additional parameters describing the reactor setup and process conditions:

PARAMETER	VALUE	DESCRIPTION
V_r	1.89 m ³	Reactor volume
v_f	3.47·10 ⁻³ m ³ /s	Volumetric flow rate
$c_{f,\text{PrO}}$	2903 mol/m ³	Concentration of PrO in feed stream
$c_{f,\text{W}}$	36291 mol/m ³	Concentration of W in feed stream
$c_{f,\text{MeOH}}$	3629 mol/m ³	Concentration of MeOH in feed stream
$c_{0,\text{W}}$	55273 mol/m ³	Initial concentration of W in the reactor
$C_{p,\text{PrO}}$	146.5 J/(mol·K)	Heat capacity of PrO
$C_{p,\text{W}}$	75.4 J/(mol·K)	Heat capacity of W
$C_{p,\text{PrOH}}$	192.6 J/(mol·K)	Heat capacity of PrOH
$C_{p,\text{MeOH}}$	81.6 J/(mol·K)	Heat capacity of MeOH
$C_{p,x}$	75.4 J/(mol·K)	Heat capacity of heat exchanger medium
$h_{\text{ref},\text{PrO}}$	-153.5·10 ³ J/mol	Enthalpy of formation of PrO at T_{ref}
$h_{\text{ref},\text{W}}$	-286.1·10 ³ J/mol	Enthalpy of formation of W at T_{ref}
$h_{\text{ref},\text{PrOH}}$	-525.6·10 ³ J/mol	Enthalpy of formation of PrOH at T_{ref}
$h_{\text{ref},\text{MeOH}}$	-238.6 J/mol	Enthalpy of formation of MeOH at T_{ref}
T_f	297 K	Feed stream temperature

PARAMETER	VALUE	DESCRIPTION
T_0	297 K	Initial reactor temperature
T_{ref}	293 K	Reference temperature
T_x	289 K	Temperature of heat exchanger medium at inlet
F_x	126 mol/s	Heat exchanger medium molar flow
UA	8441 J/(s·K)	Heat exchange parameter

The model described here is readily set up and solved using the predefined CSTR reactor type in the Reaction Engineering Lab.

Results

Figure 4-90 shows the concentration of PrO (mol/m^3) and the reactor temperature (K) as a function of reaction time.

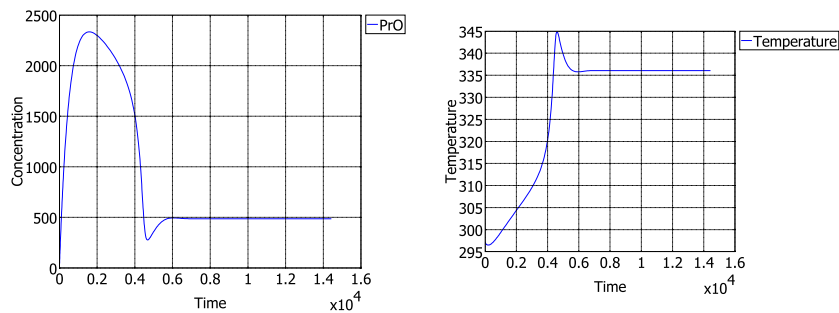


Figure 4-90: Concentrations of reactant PrO (mol/m^3) after 4 hours of operation (left) and reactor temperature (K) after 4 hours of operation (right).

Initially both the reactant concentration and the temperature oscillate around their respective steady-state values (491 mol/m^3 and 336 K , respectively). The same result

can be illustrated by a trajectory in the concentration-temperature phase plane as presented in Figure 4-91.

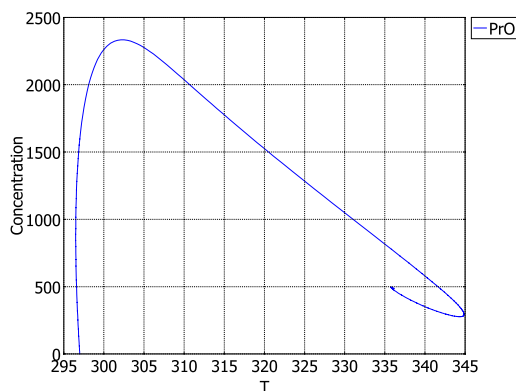


Figure 4-91: Trajectory in the concentration-temperature phase plane.

The model predicts that the reactor temperature passes a maximum value higher than the steady-state temperature. From a safety perspective it is therefore relevant to look closer at possible sets of initial conditions to see if process operation limits are violated. In the process modeled here, it is undesirable to exceed a reactor temperature of 355 K so as to avoid undesirable side reactions and not damage reactor equipment.

Figure 4-92 shows the concentration-temperature phase plane for three initial conditions; ($c_{\text{PrO}} = 0$, $T_0 = 297$), ($c_{\text{PrO}} = 0$, $T_0 = 340$), and ($c_{\text{PrO}} = 1400$, $T_0 = 340$).

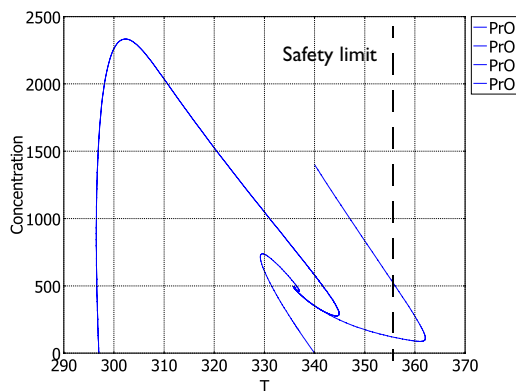


Figure 4-92: Trajectories in the concentration-temperature phase plane for three initial conditions.

The plot shows that all investigated initial conditions converge to the same steady state. However, starting with $c_{\text{PrO}} = 1400 \text{ (mol/m}^3\text{)}$ and $T_0 = 340 \text{ K}$ leads to violation of the temperature safety limits.

Reference

1. H. S. Fogler, *Elements of Chemical Reaction Engineering 3rd Ed.*, Prentice Hall PTR, 1999, Example 9-4, pp. 553–559.

Model Library path: Process_Chemistry/cstr_startup

Modeling Using the COMSOL Reaction Engineering Lab

MODEL NAVIGATOR

- 1 Start the COMSOL Reaction Engineering Lab by double-clicking its desktop icon.
- 2 In the **Model Navigator** click the **New** button.

OPTIONS AND SETTINGS

- 1 Click the **Model Settings** button on the Main toolbar.
- 2 Select **CSTR (constant volume)** from the **Reactor type** list.
- 3 Select **Liquid** from the **Reacting Fluid** list.
- 4 Select the **Calculate thermodynamic properties** check box.
- 5 Select the **Include energy balance** check box.
- 6 Go to the **Feed Streams** page.
- 7 Click the **New** button to create a reactor inlet.
- 8 Click **Close**.

Next define the constants and expressions needed later:

- 1 From the **Model** menu select **Constants**.

2 Type in the entries in the table below.

Alternatively, click the **Import Variables From File** button in the **Constants** dialog box, browse to the file `cstr_startup_const.txt` on your computer and click **Open**.

PARAMETER	VALUE	DESCRIPTION
cp_pro	146.5	Heat capacity [J/(mol*K)]
cp_w	75.4	Heat capacity [J/(mol*K)]
cp_proh	192.6	Heat capacity [J/(mol*K)]
cp_meoh	81.6	Heat capacity [J/(mol*K)]
cp_x	75.4	Heat capacity [J/(mol*K)]
href_pro	-153.5e3	Enthalphy of formation [J/mol]
href_w	-286.1e3	Enthalphy of formation [J/mol]
href_proh	-525.6e3	Enthalphy of formation [J/mol]
href_meoh	-238.6	Enthalphy of formation [J/mol]
Tref	293	Reference temperature [K]
Tf	297	Temperature of feed stream [K]
Tx	289	Temperature of heat exchanger medium [K]
Fx	126	Heat exchanger medium molar flow [mol/s]
UA	8441	Heat exchange parameter [J/(s*K)]

3 Click **OK**.

4 From the **Model** menu select **Expressions**.

5 Type in the entries in the table below.

Alternatively, click the **Import Variables From File** button in the **Expressions** dialog box, browse to the file `cstr_startup_expr.txt` on your computer and click **Open**.

PARAMETER	VALUE	DESCRIPTION
h_pro	$cp_pro \cdot (T - T_{ref}) + href_pro$	Enthalpy [J/mol]
h_w	$cp_w \cdot (T - T_{ref}) + href_w$	Enthalpy [J/mol]
h_proh	$cp_proh \cdot (T - T_{ref}) + href_proh$	Enthalpy [J/mol]
h_meoh	$cp_meoh \cdot (T - T_{ref}) + href_meoh$	Enthalpy [J/mol]
hf_pro	$cp_pro \cdot (T_f - T_{ref}) + href_pro$	Feed enthalpy [J/mol]
hf_w	$cp_w \cdot (T_f - T_{ref}) + href_w$	Feed enthalpy [J/mol]
hf_meoh	$cp_meoh \cdot (T_f - T_{ref}) + href_meoh$	Feed enthalpy [J/mol]
Q_xch	$F_x \cdot cp_x \cdot (T_x - T) \cdot (1 - \exp(-UA / (F_x \cdot cp_x)))$	Heat exchange [J/s]

6 Click **OK**.

REACTIONS INTERFACE

- 1 Click the **Reaction Settings** button on the Main toolbar.
- 2 Create a new entry in the **Reaction selection** list by clicking the **New** button.
- 3 Type $\text{PrO}+\text{W}\Rightarrow\text{PrOH}$ in the **Formula** edit field.
- 4 Select the **Use Arrhenius expressions** check box.
- 5 Type $4.71\text{e}9$ in the **A** edit field.
- 6 Type 75358 in the **E** edit field.
- 7 Type $\text{kf_1}*\text{c_PrO}$ in the **r** edit field.

SPECIES INTERFACE

- 1 While still in the **Reaction Settings** dialog box click the **Species** tab.
- 2 Verify that the **Species selection** list has the three species (**PrO**, **W**, and **PrOH**).
- 3 Click the **New** button and type MeOH in the **Formula** edit field. This adds the unreactive methanol species to the reacting mixture.
- 4 Select species **W** from the **Species selection** list and enter 55273 in the **c₀** edit field.
(Initially water is the only species present in the reactor).

At this point you associate each species with a feed stream. You also specify the associated molar concentrations and enthalpies.
- 5 Click the **Feed Stream** tab.
- 6 Select species **PrO** from the **Species selection** list, then select **Inlet I** from the **Name** list. Type 2903 in the **c_f** edit field and type hf_pro in the **h_f** edit field.
- 7 Select species **W** from the **Species selection** list, then select **Inlet I** from the **Name** list. Type 36291 in the **c_f** edit field and type hf_w in the **h_f** edit field.
- 8 Select species **MeOH** from the **Species selection** list, then select **Inlet I** from the **Name** list. Type 3629 in the **c_f** edit field and type hf_meoh in the **h_f** edit field.

Now enter thermodynamic properties for species in the reactor.
- 9 Click the **Thermo** page.
- 10 Select species **PrO** from the **Species selection** list. Type cp_pro in the **C_p** edit field and type h_pro in the **h** edit field.
- 11 Select species **W** from the **Species selection** list. Type cp_w in the **C_p** edit field and type h_w in the **h** edit field.
- 12 Select species **PrOH** from the **Species selection** list. Type cp_proh in the **C_p** edit field and type h_proh in the **h** edit field.

- I3** Select species **MeOH** from the **Species selection** list. Type **cp_meoh** in the **C_p** edit field and type **h_meoh** in the **h** edit field.

Note that you are making use of the variables you loaded previously into the **Constants** and **Expression** dialog boxes.

- I4** Click **Close**.

MODEL SETTINGS

Now return to the **Model Settings** dialog box and specify a few reactor-specific parameters.

- 1** Click the **Model Settings** button on the Main toolbar.

- 2** Go to the **Mass Balance** page.

- 3** Type **1.89** in the **V_r** edit field and type **0** in the **v_p** edit field.

The **Volumetric production rate** edit field contains a predefined expression that accounts for any volume change due to chemical reaction. In this example you assume that the density of the reacting mixture is constant and thus set the value to zero.

- 4** Go to the **Energy Balance** page.

- 5** Type **Q_xch** in the **Q_{ext}** edit field.

This sets the external heat source term equal to the expression in the **Expressions** dialog box.

- 6** Go to the **Feed Streams** page.

- 7** Select **Inlet1** from the list to the left.

- 8** Type **3.47e-3** in the **v_f** edit field and type **Tf** in the **T_f** edit field.

- 9** Go to the **Init** page.

- 10** Type **297** in the **T(t₀)** edit field.

- 11** Click **Close**.

COMPUTING THE SOLUTION

- 1** Open the **Simulation>Solver Parameters** dialog box.

- 2** Type **4*3600** in the **Times** edit field.

- 3** Clear the **Stop if steady state is reached first** check box.

- 4** Click **OK**.

- 5** Click the **Solve Problem** button (=) on the Main toolbar.

POSTPROCESSING AND VISUALIZATION

The default plot shows the concentrations of all participating species as a function of time. To create the figures that appeared in the Results section follow these steps:

- 1 Choose **Postprocessing>Plot Parameters** (or click the corresponding button on the Main toolbar).
- 2 Click the << button to remove all entries from the **Quantities to plot** list.
- 3 Select **PrO** from the **Predefined quantities** list and click the **Add Selected Predefined Quantities** button, >.
- 4 Select **New Figure** from the **Plot in** list.
- 5 Click **Apply** to create the left panel of Figure 4-90.
- 6 Click the << button to remove all entries from the **Quantities to plot** list.
- 7 Select **Temperature** from the **Predefined quantities** list and click the **Add Selected Predefined Quantities** button, >.
- 8 Select **New Figure** from the **Plot in** list.
- 9 Click **Apply** to create the right panel of Figure 4-90.
- 10 Click the << button to remove all entries from the **Quantities to plot** list.
- 11 Select **PrO** from the **Predefined quantities** list and click the **Add Selected Predefined Quantities** button, >.
- 12 Select the **Expression** option button in the **x-axis data** area and click the **Expression** button.
- 13 Select **Temperature** from the **Predefined quantities** list and click **OK**.
- 14 Select **New Figure** from the **Plot in** list.
- 15 Select **Keep current plot** and click **OK** to create Figure 4-91.

Now change the initial conditions, re-solve the model, and plot the results.

- 1 Click the **Model Settings** button on the Main toolbar.
- 2 Go to the **Init** page.
- 3 Type 340 in the **T(t₀)** edit field.
- 4 Click **Close**.
- 5 Click the **Solve Problem** button on the Main toolbar.

Note how the new results are plotted in the **Figure 3** window on top of the previous results.

- 6 Click the **Reaction Settings** button on the Main toolbar.

- 7 Go to the **Species>General** page.
- 8 Select species **PrO** from the **Species selection** list and enter 1400 in the **c₀** edit field.
- 9 Click **Close**.
- 10 Click the **Solve Problem** button on the Main toolbar.

The plot in the **Figure 3** window now represents Figure 4-92 in the Results section of this model.

Fluid Catalytic Cracking

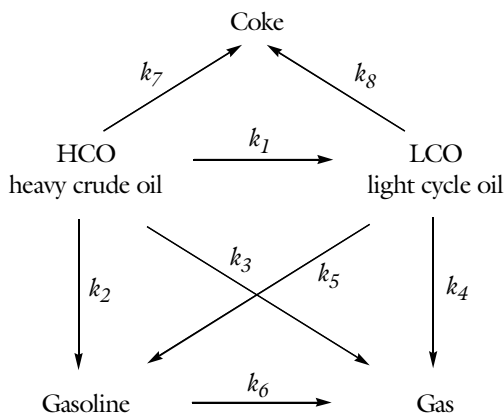
Introduction

This example illustrates the fluid catalytic cracking (FCC) of a flashed distillate feedstock occurring in plug-flow reactor. The simulations consider how coking affects the catalytic activity and selectivity in the process.

The model shows you how to set up a reaction kinetic network in the Reaction Engineering Lab. As you type in the chemical reaction formulas in the graphical user interface, the software automatically generates the corresponding rate expressions. In a first simulation you can directly make use of the automatically generated kinetics to model the FCC process in an ideal reactor system. In a second simulation, you can extend the kinetic model to include the effects of catalyst coking.

Model Description

The complex chemistry involved in FCC is often reduced to kinetic models where reactants and products are lumped together in different hydrocarbon groups. A five-lump model for the catalytic cracking of a hydrotreated flash distillate has been proposed in the literature (Ref. 1):



All 8 reactions follow first order kinetics:

$$r_j = k_j c_i \quad j = 1, \dots, 8 \quad (4-187)$$

A first model looks at the cracking reactions, neglecting coking (reactions 7 and 8). The reactor model is an ideal plug-flow reactor running at constant temperature (798 K), described by the following mass balance:

$$\frac{dF_i}{dV} = \sum_j v_{ij} r_j = R_i \quad (4-188)$$

where F_i is the species molar flow rate, V the reactor volume, v_{ij} is the stoichiometric coefficient, and r_j the reaction rate.

Assuming constant reactor cross section and flow velocity, the species concentration gradient as function of residence time (τ) is given by:

$$\frac{dF_i}{dV} = \frac{d(vc_i)}{dV} = \frac{dc_i}{d\tau} = R_i \quad (4-189)$$

KINETICS DISREGARDING COKING

Neglecting the coke producing reactions 7 and 8, the detailed mass balances with respect to the lumped species become:

$$\frac{dc_{\text{hco}}}{d\tau} = -r_1 - r_2 - r_3 \quad (4-190)$$

$$\frac{dc_{\text{lco}}}{d\tau} = r_1 - r_4 - r_5 \quad (4-191)$$

$$\frac{dc_{\text{gasoline}}}{d\tau} = r_2 + r_5 - r_6 \quad (4-192)$$

$$\frac{dc_{\text{gas}}}{d\tau} = r_3 + r_4 + r_6 \quad (4-193)$$

The Reaction Engineering Lab automatically sets up Equation 4-190 through Equation 4-193 as you type in the chemical reaction formulas into the graphical user interface.

KINETICS INCLUDING COKING

In a second simulation you will include coking reactions into the kinetic model, which affect both selectivity as well as activity. The overall activity of the system is dominated by two different time scales. Coke formation occurs on the millisecond scale, while the

formation of other products takes place in seconds. To account for these different time scales, two different activity functions are used.

For the non-coking reactions (reactions 1 through 6) the activity function is given by:

$$a = e^{-k_d c_c} \quad (4-194)$$

where k_d is a deactivation constant and C_C the coke content of the catalyst. The reaction rates are modified by the activity according to:

$$r_j = a k_j c_i \quad j = 1, \dots, 6 \quad (4-195)$$

For the coking reactions (reactions 7 and 8), the activity function is:

$$b = e^{-\alpha \tau} \quad (4-196)$$

where α is a deactivation constant depending on the residence time. The reaction rates become:

$$r_j = b k_j c_i \quad j = 7, 8 \quad (4-197)$$

The reactor mass balances are:

$$\frac{dc_{\text{hco}}}{d\tau} = -r_1 - r_2 - r_3 - r_7 \quad (4-198)$$

$$\frac{dc_{\text{lco}}}{d\tau} = r_1 - r_4 - r_5 - r_8 \quad (4-199)$$

$$\frac{dc_{\text{gasoline}}}{d\tau} = r_2 + r_5 - r_6 \quad (4-200)$$

$$\frac{dc_{\text{gas}}}{d\tau} = r_3 + r_4 + r_6 \quad (4-201)$$

$$\frac{dc_{\text{coke}}}{d\tau} = r_7 + r_8 \quad (4-202)$$

You can readily include the effect of catalyst deactivation by modifying the automatically generated kinetics in the Reaction Engineering Lab.

Results

Figure 4-93 shows the concentrations of the lumped components as functions of the residence time. The upper graph illustrates the results when the coking reactions are ignored, while the lower results include the effect of coking.

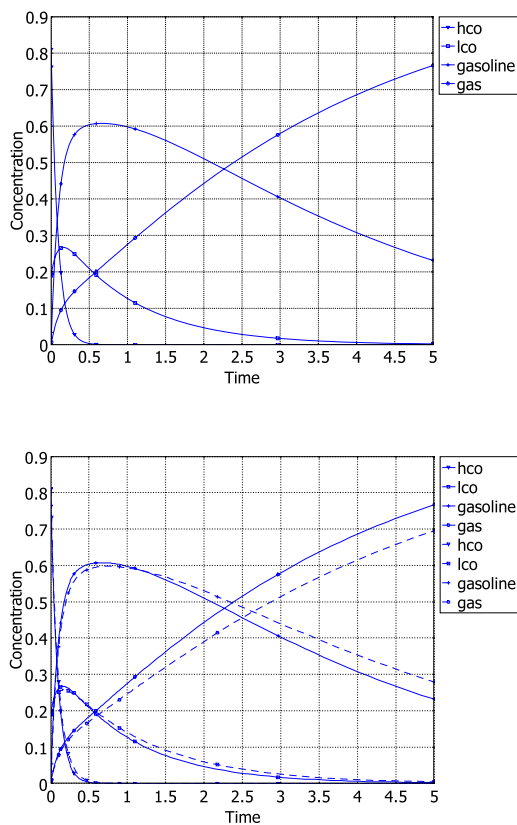


Figure 4-93: Concentrations of lumped species as function of the reactor residence time. Results are displayed for models where coking is ignored (solid lines), and where coking is taken into account (dashed lines).

The results show a clear influence of coking on the product distribution, in this case favoring gasoline production relative to the fraction of gas.

Figure 4-94 shows the concentration of coke along with the activity functions for non-coking reactions (Equation 4-194), and coking reactions (Equation 4-196).

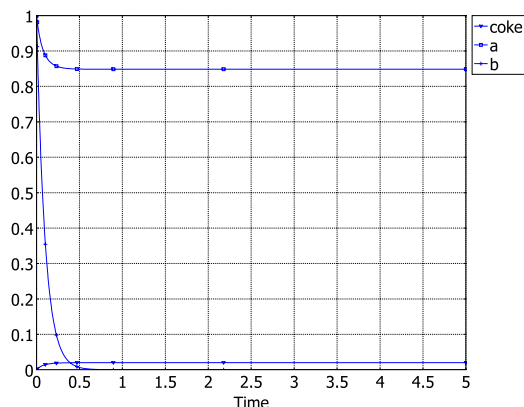


Figure 4-94: Concentration profile of coke, as well as activity functions for non-coking reactions (a), and coking reactions (b).

The activity function, b , limits the effect of the coking reactions to relatively short residence times. Once the deposition of carbon has stopped, the activity for the non-coking reactions remains constant at ~ 0.85 .

Reference

1. M. A. den Hollander, M. Wissink, M. Makkee, J. A. Moulijn, *J. Appl. Catal. A*, vol. 223, p. 103, 2003.

Model Library path: Process_Chemistry/catalytic_cracking

Modeling Using the COMSOL Reaction Engineering Lab

MODEL NAVIGATOR

- 1 Start the **COMSOL Reaction Engineering Lab** by double-clicking its desktop icon.
- 2 In the **Model Navigator** click the **New** button.

REACTIONS INTERFACE

- 1 From the **Model** menu select **Reaction Settings**.
- 2 Create six entries in the **Reaction selection** list by clicking the **New** button.
- 3 Enter the reaction formulas as shown in the following table by first selecting the appropriate row in the **Reaction selection** list and then entering the text in the corresponding **Formula** edit field.

REACTION ID #	REACTION FORMULA
1	$\text{hco} \Rightarrow \text{lco}$
2	$\text{hco} \Rightarrow \text{gasoline}$
3	$\text{hco} \Rightarrow \text{gas}$
4	$\text{lco} \Rightarrow \text{gas}$
5	$\text{lco} \Rightarrow \text{gasoline}$
6	$\text{gasoline} \Rightarrow \text{gas}$

- 4 Enter the following values for the **Forward rate constant** by first selecting the appropriate row in the **Reaction selection** list and then entering the corresponding number in the k^f edit field:

REACTION ID #	k^f
1	1.9
2	7.5
3	1.5
4	0
5	1
6	0.3

SPECIES INTERFACE

- 1 While still in the **Reaction Settings** dialog box, click the **Species** tab.
- 2 Verify that the **Species selection** list contains four species (**hco**, **lco**, **gasoline**, and **gas**).
- 3 On the **General** page, enter the following initial concentrations in the c_0 edit field after selecting the appropriate entry in the **Species selection** list:

SPECIES NAME	c_0
hco	0.81
lco	0.19

SPECIES NAME	c_0
gasoline	0
gas	0

4 Click **Close**.

COMPUTING THE SOLUTION

- 1 Click the **Solver Parameters** button on the Main toolbar.
- 2 Enter 5 in the **Times** edit field. The units here are in seconds.
- 3 Click **OK**.
- 4 Click the **Solve Problem** button (=) on the Main toolbar.

POSTPROCESSING AND VISUALIZATION

The default plot shows the time variation of the concentration of all species. Now, include the coking reactions in the existing kinetics.

REACTIONS INTERFACE

- 1 Click the **Reaction Settings** button on the Main toolbar.
- 2 Go to the **Reactions** page.
- 3 Create two new entries in the **Reaction selection** list by clicking the **New** button twice.
- 4 Enter the reaction formulas as shown in the following table:

REACTION ID #	REACTION FORMULA
7	$\text{hco} \Rightarrow \text{coke}$
8	$\text{lco} \Rightarrow \text{coke}$

- 5 Enter the following values for the **Forward rate constant** by first selecting the appropriate row in the **Reaction selection** list and then entering the corresponding number in the k^f edit field:

REACTION ID #	k^f
7	0.21
8	0.5

Up until this point, all kinetic expressions for the reaction rates have been automatically generated by the software. Now, you will modify the existing expressions to include the activity functions, Equation 4-194 and Equation 4-196.

- 6 Modify the existing reaction rate expressions according to the following table by first selecting the appropriate row in the **Reaction selection** list and then entering the text in the corresponding **Reaction rate** edit field.

In practice you are multiplying the first six reactions with the variable a, and the last two reactions by the variable b.

REACTION ID #	REACTION RATE
1	$kf_1 \cdot c_hco \cdot a$
2	$kf_2 \cdot c_hco \cdot a$
3	$kf_3 \cdot c_hco \cdot a$
4	$kf_4 \cdot c_lco \cdot a$
5	$kf_5 \cdot c_lco \cdot a$
6	$kf_6 \cdot c_gasoline \cdot a$
7	$kf_7 \cdot c_hco \cdot b$
8	$kf_8 \cdot c_lco \cdot b$

- 7 Click **Close**.

OPTIONS AND SETTINGS

Now, define the activity functions corresponding to the variables a (Equation 4-194), and b (Equation 4-196).

- 1 From the **Model** menu select **Expressions**.
- 2 Enter the following parameter names and values in the **Expressions** dialog box:

NAME	EXPRESSION	DESCRIPTION
a	$\exp(-kd \cdot c_coke)$	activity function for non-coking reactions
b	$\exp(-\alpha \cdot t)$	activity function for coking reactions
kd	8.2	deactivation constant
alfa	10	deactivation constant

- 3 Click **OK**.

POSTPROCESSING AND VISUALIZATION

- 1 Click the **Plot Parameters** button on the Main toolbar.
- 2 From the **Plot in** list, select **New Figure**.
- 3 Select the **Keep current plot** check box

4 Click **OK**.

COMPUTING THE SOLUTION

1 Click the **Solve Problem** button (=) on the Main toolbar.

POSTPROCESSING AND VISUALIZATION

Return to plotting in the main user interface and visualize the results of the coking and its effect on catalytic activity.

1 Select the menu item **Postprocessing>Plot Parameters**.

2 From the **Plot in** list, select **Main axes**.

3 Clear the **Keep current plot** check box.

4 Remove all entries in the **Quantities to plot** list by pressing the << button.

5 Select **coke** in the **Predefined quantities** list and press the > button.

6 Type a in the **Expressions** edit field and press the > button.

7 Type b in the **Expressions** edit field and press the > button.

8 Click **OK**.

Carbon Deposition in Heterogeneous Catalysis

Introduction

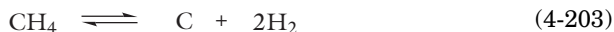
Carbon deposition onto the surface of solid catalysts is commonly observed in hydrocarbon processing. Carbon deposits can affect both the activity of catalysts as well as the flow of gas through a catalyst bed.

This example investigates the thermal decomposition of methane into hydrogen and solid carbon. In the first model you look at the isothermal process occurring in an ideal reactor, simulated in the Reaction Engineering Lab. The influence of carbon deposition on catalyst activity is also considered. In the second model, you study the effect that the carbon deposits have on the fluid flow. The second simulation takes place in COMSOL Multiphysics taking both time and space dependencies into account.

Model Definition

CHEMISTRY

Methane decomposes over a Ni/Al₂O₃ catalyst according to the overall chemical reaction:



The following reaction rate expression has been reported in the literature (Ref. 1).

$$r = k \cdot \frac{p_{\text{CH}_4} - \frac{p_{\text{H}_2}^2}{K_p}}{(1 + k_H \sqrt{p_{\text{H}_2}})^2} \quad (4-204)$$

where

$$k = \exp\left(20.492 - \frac{104200}{R_g T}\right) \quad (4-205)$$

$$k_H = \exp\left(\frac{163200}{R_g T} - 22.426\right) \quad (4-206)$$

and

$$K_p = 5.088 \cdot 10^5 \cdot \exp\left(-\frac{91200}{R_g T}\right) \quad (4-207)$$

IDEAL REACTOR MODEL

The first model is set up in Reaction Engineering Lab. This treats the isothermal decomposition of methane (Equation 4-203) in a perfectly mixed reactor with constant volume. The species mass balances are summarized by:

$$\frac{dc_i}{dt} = R_i \quad (4-208)$$

The rate term, R_i , takes into account the reaction stoichiometry, v_i , the reaction rate, r , and the catalyst activity, a :

$$R_i = v_i r a \quad (4-209)$$

The mass balances of the reacting species are then:

$$\frac{dc_{CH_4}}{dt} = -ra \quad (4-210)$$

$$\frac{dc_C}{dt} = ra \quad (4-211)$$

$$\frac{dc_{H_2}}{dt} = 2ra \quad (4-212)$$

The time dependency of the catalytic activity is expressed by the ODE:

$$\frac{da}{dt} = -k_a r^2 c_C a \quad (4-213)$$

where

$$k_a = \exp\left(\frac{135600}{R_g T} - 32.007\right) \quad (4-214)$$

Solving the mass balances provides the evolution of the species concentrations over time. The fact that carbon is in the solid phase is taken into account by removing its effect on gas phase physical properties. The pressure in the reactor is a function of only the methane and hydrogen concentrations:

$$p = R_g T (c_{\text{CH}_4} + c_{\text{H}_2}) \quad (4-215)$$

SPACE- AND TIME-DEPENDENT MODEL

The second model is solved in COMSOL Multiphysics and takes both fluid flow and the chemical reaction into account.

The flow reactor is set up in 2D, as illustrated below:

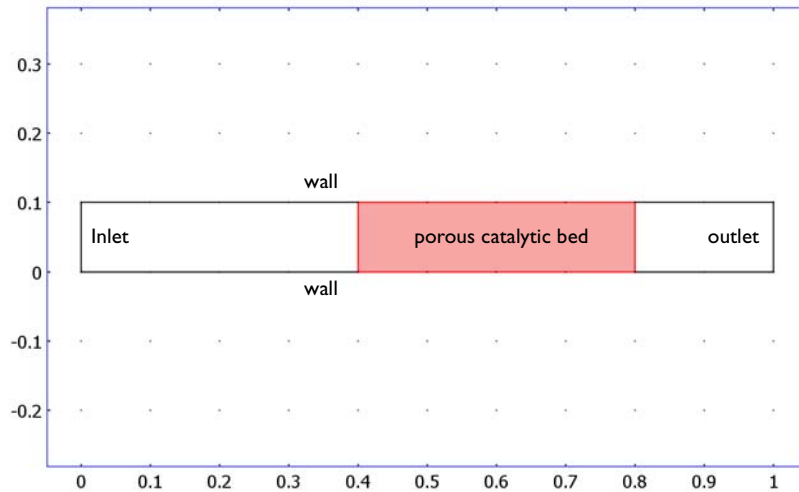


Figure 4-95: A flow reactor is set up in 2D. Methane enters from the left and reacts in the porous catalytic bed in the mid-section of the geometry.

Methane first flows through a free section of the reactor, and then encounters a porous catalytic bed where the decomposition reaction takes place.

Momentum Balances

The flow in the free channel section is described by the Navier-Stokes equations:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \nabla \cdot [-\eta(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) + p\mathbf{I}] = -\rho(\mathbf{u} \cdot \nabla)\mathbf{u} \quad (4-216)$$

$$\nabla \cdot \mathbf{u} = 0$$

where ρ denotes density (kg/m^3), \mathbf{u} represents the velocity (m/s), η denotes viscosity ($\text{kg}/(\text{m} \cdot \text{s})$), and p equals pressure (Pa). In the porous domain, the Brinkman equations govern the flow:

$$\frac{\rho}{\varepsilon_p} \frac{\partial \mathbf{u}}{\partial t} + \nabla \cdot \left[-\frac{\eta}{\varepsilon_p} (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) + p \mathbf{I} \right] = -\frac{\eta}{k} \mathbf{u} \quad (4-217)$$

$$\nabla \cdot \mathbf{u} = 0$$

where ε_p is the porosity and k denotes permeability (m^2) of the porous media. As you can see in Equation 4-216 and Equation 4-217, the momentum-balance equations are closely related. The term on the right-hand side of the Navier-Stokes formulation corresponds to momentum transported by convection in free flow. In the Brinkman formulation, this term is replaced by a contribution associated with the drag force experienced by the fluid as it flows through a porous medium. COMSOL Multiphysics automatically combines free and porous-media flow to solve the equations simultaneously.

The boundary conditions for the flow are:

$$\begin{aligned} \mathbf{u} \cdot \mathbf{n} &= u_0 && \text{inlet} \\ \mathbf{u} &= \mathbf{0} && \text{walls} \\ p &= 0 && \text{outlet} \end{aligned} \quad (4-218)$$

Mass transport in the reactor is described by the diffusion-convection equations:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i + c_i \mathbf{u}) = R_i \quad (4-219)$$

where D_i denotes the diffusion coefficient (m^2/s) and c_i is the species concentration. The term R_i corresponds to the species' net reaction rates.

In the free channel, the inlet conditions are equal to the inlet concentrations

$$c = c_{\text{in}} \quad (4-220)$$

At the outlet, you use the convective flux condition

$$\mathbf{n} \cdot (-D \nabla c) = 0 \quad (4-221)$$

All other boundaries use the insulating or symmetry condition

$$\mathbf{n} \cdot (-D \nabla c + c \mathbf{u}) = 0 \quad (4-222)$$

Balance for Void Fraction

The void fraction of the catalytic bed decreases as carbon is deposited. This in turn affects the flow through the reactor. A balance for the void fraction, or porosity, of the bed is given by:

$$\frac{d\varepsilon}{dt} = -\frac{\varepsilon r}{M_c \rho_{\text{soot}}} \quad (4-223)$$

This equation can be implemented in the PDE, General Form application mode of COMSOL Multiphysics, resulting in porosity distribution across the catalytic bed as a function of time. The initial porosity of the bed is assumed to be $\varepsilon = 0.4$.

The porosity is related to the permeability of the porous domain by the expression (Ref. 2):

$$k = k_0 \left(\frac{\varepsilon}{\varepsilon_0} \right)^{3.55} \quad (4-224)$$

In this way, the porosity balance couples the mass and momentum balances describing the reacting system.

Results

IDEAL REACTOR MODEL

The upper graph of Figure 4-96 shows the concentration transients of methane, hydrogen and deposited carbon, as methane decomposes over a Ni/Al₂O₃ catalyst.

The lower graph is a plot of the reactor pressure. Deactivation of the catalyst is not taken into account at this point.

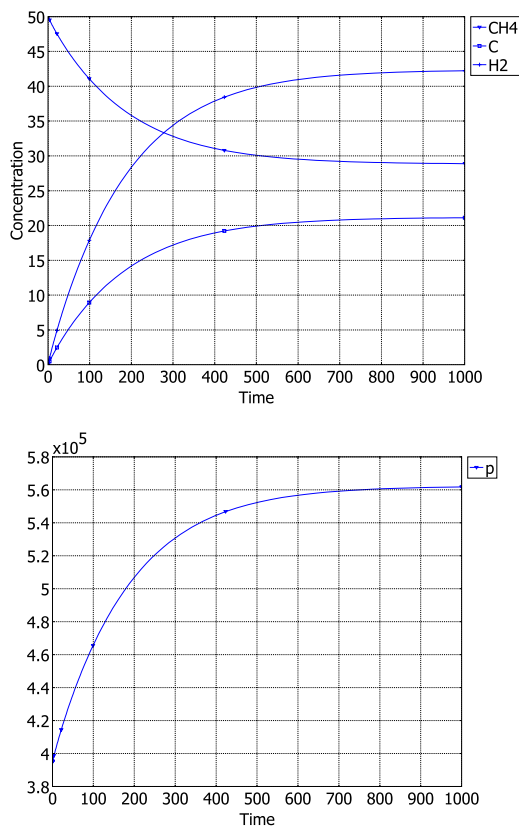


Figure 4-96: Upper graph: concentration transients of methane decomposition over a Ni/ Al_2O_3 catalyst. Lower graph: reactor pressure. Deactivation of the catalyst is not considered.

Taking catalyst deactivation into account (Equation 4-213) produces the results shown in Figure 4-97. Under the simulated conditions a moderate drop in activity is

noted (upper graph), leading to a largely unaffected overall process, as can be seen by comparing with the concentration transients of the previous model (lower graph).

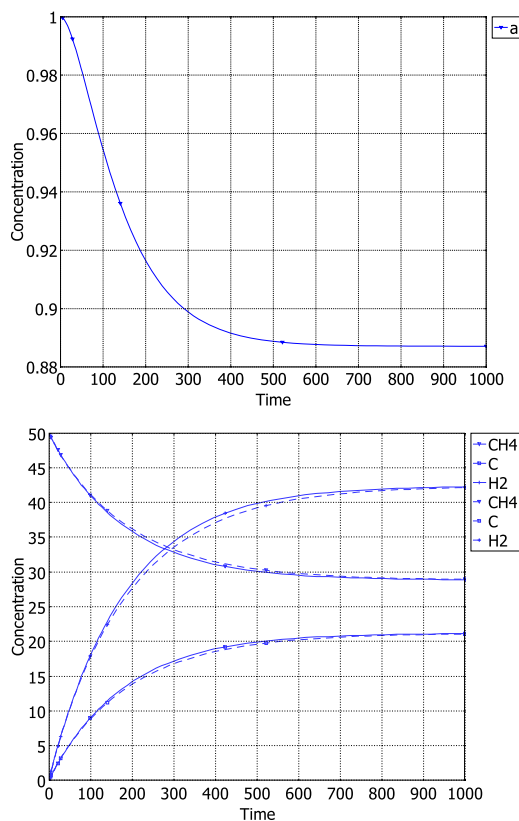


Figure 4-97: Upper graph: catalyst activity drops off as carbon deposits at the catalyst surface. Lower graph: concentration transients of methane, hydrogen and deposited carbon with no deactivation present (solid lines) and with deactivation taken into account (dashed lines).

SPACE- AND TIME-DEPENDENT MODEL

The following results concern a space- and time-dependent model simulated in COMSOL Multiphysics. Methane decomposition occurs in a porous region where solid catalyst particles are packed. Figure 4-98 shows the velocity field across the reactor prior to carbon deposition. The 2D plot shows that the velocity profile is parabolic in the free channel sections and close to constant in the porous domain. The

line plot in the bottom graph in Figure 4-98 shows the velocity along the reactor centerline.

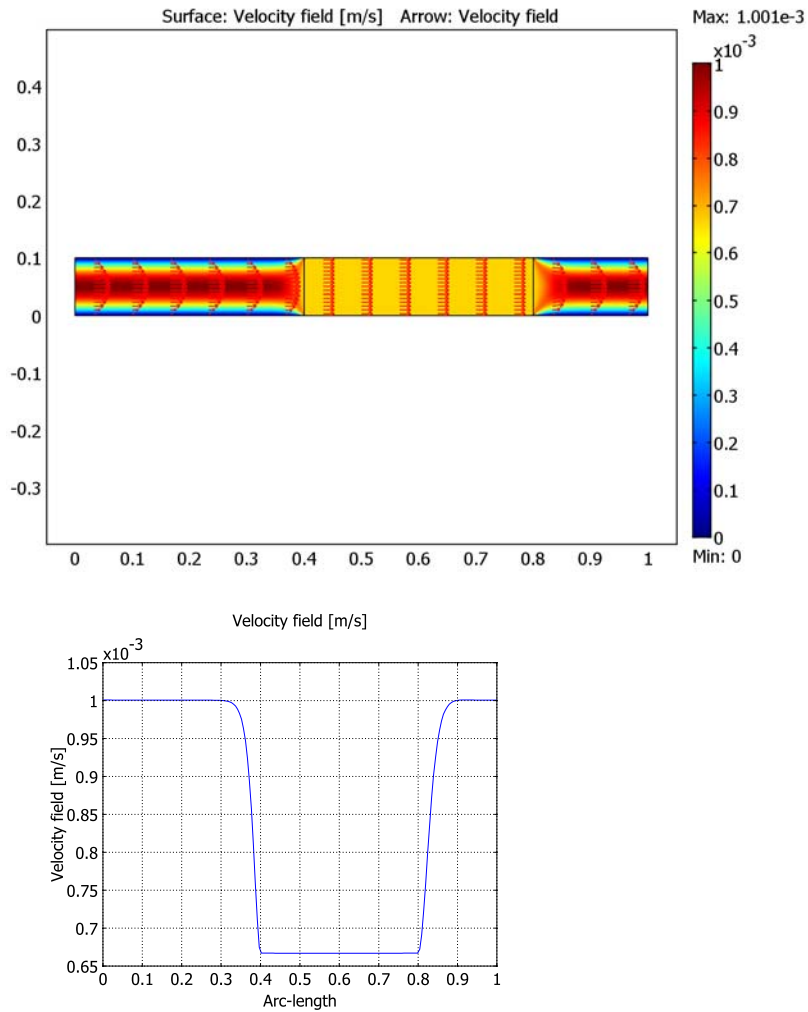


Figure 4-98: Upper graph: velocity flow field in the 2D reactor domain. Lower graph: the gas velocity plotted along the reactor centerline.

Reactions take place in the packed catalytic bed located in the mid section of the reactor. Figure 4-99 shows the concentration profiles along the centerline of the bed.

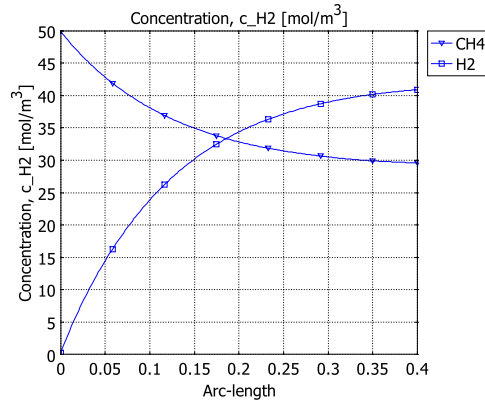


Figure 4-99: Methane and hydrogen concentrations as a function of the bed position.

The methane and hydrogen concentrations are equal after passing approximately 0.18 m into the bed. Figure 4-98 shows that the velocity in the bed is near $0.67 \cdot 10^{-3}$ m/s, equaling a residence time of 270 s. This result agrees with the findings from the ideal reactor simulation, shown in Figure 4-96.

Now, consider the effects as methane is constantly supplied to the reactor for 1000 seconds. The initial permeability is a constant $1 \cdot 10^{-9}$ m² across the bed. Note how the permeability at the front end of the bed changes by four orders of magnitude during the first 1000 s of carbon deposition.

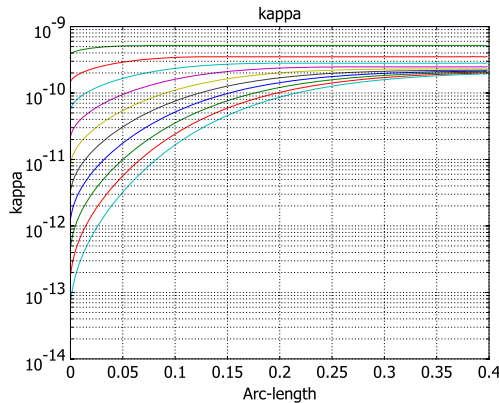


Figure 4-100: Permeability of the packed catalytic bed as the decomposition of methane proceeds for 1000 s. The time interval between each line is 100 s.

As carbon deposits in the reacting bed, the pressure distribution across the reactor is affected. Figure 4-101 shows a small, linear pressure drop as unreacting gas passes through a clean catalyst bed.

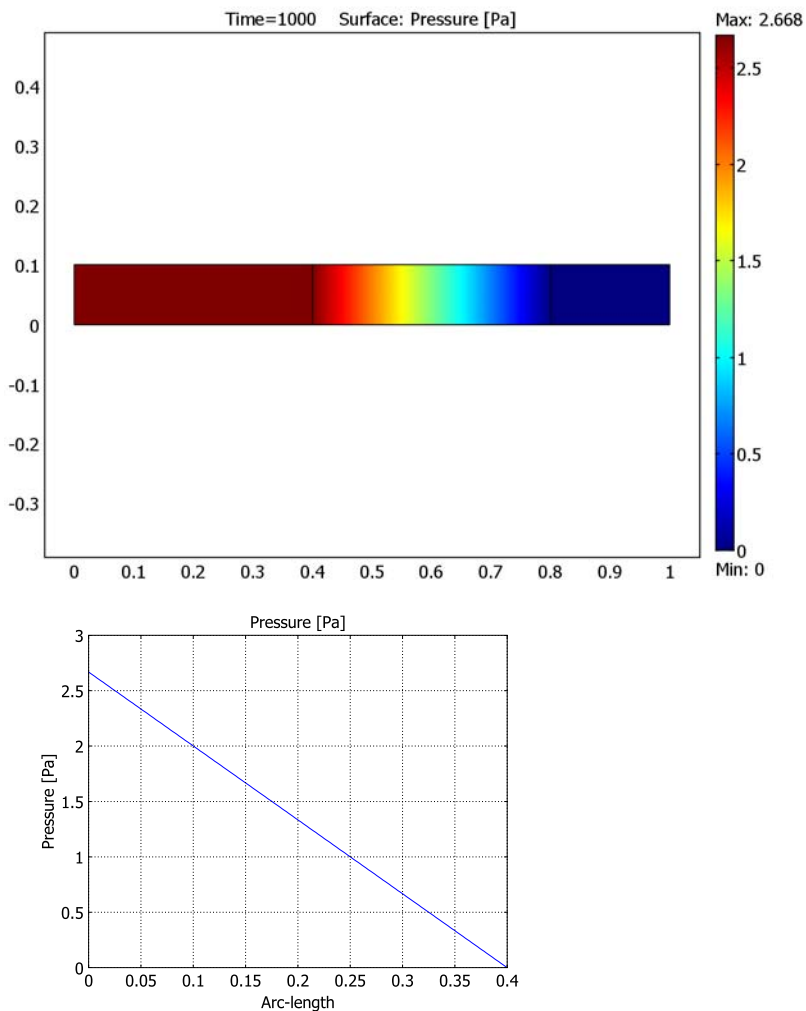


Figure 4-101: Distribution of pressure as an unreacting gas passes a clean catalyst bed. Upper graph: pressure distribution across the 2D reactor domain. Lower graph: pressure drop along the packed catalyst bed.

Figure 4-102 shows the pressure distribution across the reactor after methane decomposition has occurred for 1000 s. The pressure drop is notably greater and occurs across the first 10 cm of the bed.

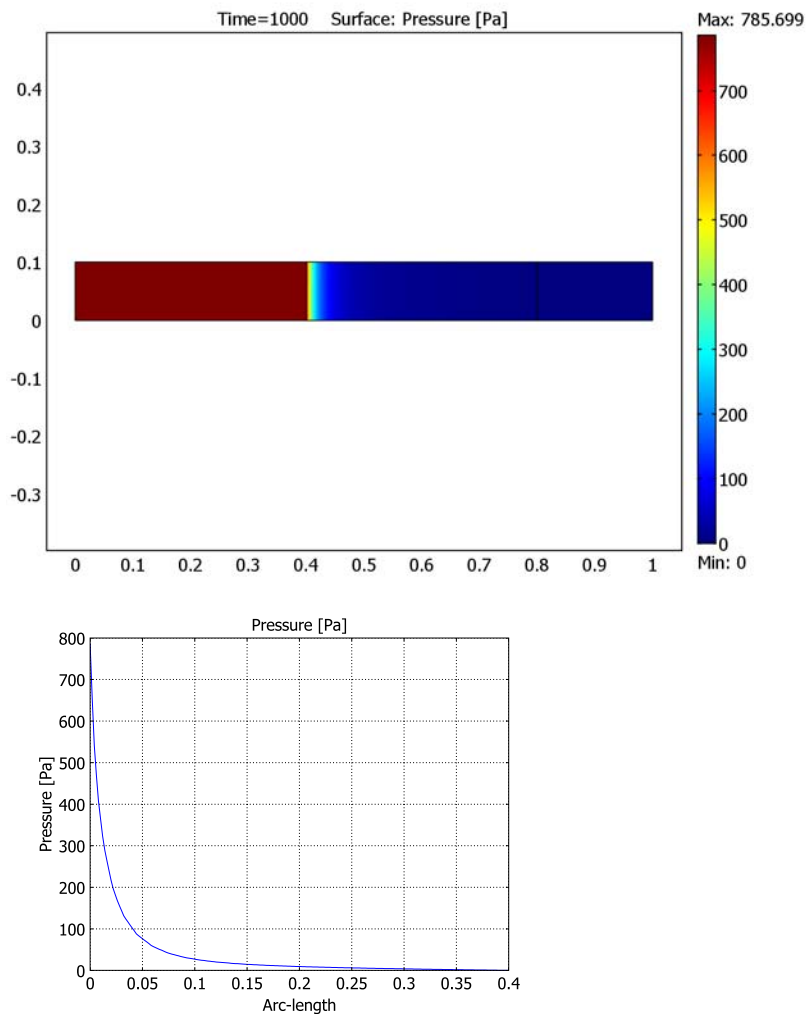


Figure 4-102: Distribution of pressure when methane decomposition has been allowed to occur for 1000 s. Upper graph: pressure distribution across the 2D reactor domain. Lower graph: pressure drop along the packed catalyst bed.

References

1. S.G. Zavarukhin and G.G. Kuvshinov, *J. Appl. Catal. A*, vol. 272, p. 219, 2004.
2. E.A. Borisova and P.M. Adler, *Phys. Rev. E*, vol. 71, p. 016311-1, 2005.

The following path shows the location of the Reaction Engineering Lab model:

Model Library path: Process_Chemistry/carbon_deposition

The following path shows the location of the COMSOL Multiphysics model:

Model Library path: Reaction_Engineering_Lab/Process_Chemistry/
carbon_deposition

Modeling Using the COMSOL Reaction Engineering Lab

MODEL NAVIGATOR

- 1 Start COMSOL Reaction Engineering Lab.
- 2 Click **New** in the **Model Navigator** window.

REACTIONS INTERFACE

- 1 Click the **Reaction Settings** button on the Main toolbar.
- 2 Make sure the **Reactions** page is active. Create a new entry in the **Reaction selection** list by clicking the **New** button.
- 3 Type $\text{CH}_4 \Rightarrow \text{C} + 2\text{H}_2$ in the **Formula** edit field.
- 4 Modify the predefined reaction rate according to Equation 4-204 by typing the following in the **r** edit field: $c_a * k * (p_{\text{CH}_4} - p_{\text{H}_2}^2 / K_p) / (1 + k_h * \sqrt{p_{\text{H}_2}})^2$.
You will define the parameters and constants for the rate expression later on.

SPECIES INTERFACE

- 1 Click the **Species** tab.
- 2 Create a new entry in the **Species selection** list by clicking the **New** button.

- 3 Type **a** in the **Formula** edit field.

When a new species is created a mass balance equation is set up along with it, in this case:

$$\frac{dc_a}{dt} = R_a$$

The left hand side is defined internally in the software and the right hand side corresponds to the expression given in the **R** edit field.

Note also that you can remove the effect of catalyst activity from your model by selecting the **Lock concentration/activity** check box. This removes the species mass balance and sets the concentration of the species to the value entered in the **Initial concentration** edit field.

- 4 Proceed to define the equation for the catalyst activity (Equation 4-213) by selecting species **a** from the **Species selection** list and typing $-k_a \cdot r_1^2 \cdot c_C \cdot c_a$ in the **R** edit field.
- 5 Select the appropriate entry from the **Species selection** list and then enter the corresponding value for the **Initial concentration**:

SPECIES NAME	c0
CH4	50
a	1

- 6 Click **Close**.

OPTIONS AND SETTINGS

- 1 Click the **Model Settings** button on the Main toolbar.
- 2 On the **General** page type 950 in the **Temperature** edit field.
- 3 In the **p** edit field, modify the predefined expression for the pressure to:
 $R_g \cdot T \cdot (c_{CH4} + c_{H2})$.

The predefined expression for the pressure in the reactor is:

$$p = R_g T \sum c_i$$

You remove the contributions from the carbon species and the activity parameter, as they do not contribute to the gas phase pressure.

- 4 Click **Close**.
- 5 Select the menu item **Model>Expressions**.

- 6 Enter the following expressions by typing them in. Alternatively, click the **Import Variables From File** button and browse to the file:
carbon_deposition_expressions.txt:

NAME	EXPRESSION	DESCRIPTION
k	$2.31e-5 \cdot \exp(20.492 - 104200/R_g/T)$	Arrhenius expression
Kp	$5.088e5 \cdot \exp(-91200/R_g/T)$	Arrhenius expression
kh	$\exp(163200/R_g/T - 22.426)$	Arrhenius expression
ka	$43240 \cdot \exp(135600/R_g/T - 32.077)$	Arrhenius expression
p_CH4	c_CH4*Rg*T/100000	CH4 pressure (bar)
p_H2	c_H2*Rg*T/100000+eps	H2 pressure (bar)

- 7 Click **OK**.

COMPUTING THE SOLUTION

- 1 Click the **Solver Parameters** button on the Main toolbar.
- 2 Type 1000 in the **Times** edit field.
- 3 Click **OK**.
- 4 Compute the solution by clicking the **Solve Problem** button on the Main toolbar.

EXPORT SETTINGS

You will now export the reaction model from Reaction Engineering Lab to COMSOL Multiphysics, and see how the chemistry of methane decomposition behaves in a time and space dependent system. The COMSOL Multiphysics model assumes that the catalyst activity is constant. The deposition of carbon, however, affects reactor performance because the deposits affect the permeability of the porous section of the reactor.

- 1 Click the **Reaction Settings** button on the Main toolbar.
- 2 Go to the **Species** page.
- 3 Select the **a** from the **Species selection** list and select the **Lock concentration/activity** check box.

The activity is assumed to be constant and equal to one.

- 4 Select the species **C** from the **Species selection** list and then select the **Lock concentration/activity** check box.

The purpose of this setting is to avoid the automatic set up of a mass balance equation for the species C in COMSOL Multiphysics. The effect of the carbon deposition rate will be taken into account by a balance equation for the reactor bed void fraction (Equation 4-223), that will be set up after the export.

- 5 Click **Close**.
- 6 Click the **Export to COMSOL Multiphysics** button on the Main toolbar.
- 7 Select **2D** from the **Space dimension** list and click **OK**.
- 8 The **Export to COMSOL Multiphysics** dialog box appears.
- 9 Go to the **Export mass balance** area, and in the **Application mode** list select **Convection and Diffusion: New**.
- 10 In the **Group name** edit field type reactions.
- 11 Move to the **Export energy balance** area and clear the check box in the upper left corner.
- 12 Move to the **Export momentum balance** area and clear the check box in the upper left corner.
- 13 Click the **Export** button at the bottom of the dialog box.

Modeling Using COMSOL Multiphysics

Click the **COMSOL Multiphysics** window.

MODEL NAVIGATOR

- 1 Select the menu item **Multiphysics>Model Navigator**.
- 2 In the **Application Modes** tree, select **Chemical Engineering Module>Momentum Transport>Laminar Flow>Incompressible Navier-Stokes**.
- 3 Click the **Add** button.
- 4 In the **Application Modes** tree, select **COMSOL Multiphysics>PDE Modes>PDE, General Form**.
- 5 Type por in the **Dependent variables** edit field, then click the **Add** button.
- 6 Click the **OK** button.

GEOMETRY MODELING

- 1 Press the Shift key and click the **Rectangle/Square** button.

- 2 Type the following values in the corresponding edit fields for the rectangle dimensions.

SIZE		POSITION	
Width	1	x	0
Height	0.1	y	0

- 3 Click **OK**.
- 4 Press the Shift key again and click the **Rectangle/Square** button.
- 5 Type the following values in the corresponding edit fields for the rectangle dimensions

SIZE		POSITION	
Width	0.4	x	0.4
Height	0.1	y	0

- 6 Click **OK**.
- 7 Click the **Zoom Extents** button on the Main toolbar.

PHYSICS SETTINGS

Subdomain Settings—Navier-Stokes Application Mode

- 1 Select **Incompressible Navier-Stokes (chns)** from the **Multiphysics** menu.
- 2 Select **Subdomain Settings** from the **Physics** menu.
- 3 Select all subdomains by pressing Ctrl+A and clicking the **Subdomain selection** list.
- 4 Type 1 in the **Density** edit field.
- 5 Type $1e-5$ in the **Dynamic viscosity** edit field.
- 6 Select Subdomain 2 (the porous media subdomain) from the **Subdomain selection** list.
- 7 Select the **Flow in porous media (Brinkman equations)** check box.
- 8 Type por in the **Porosity** edit field.
- 9 Type kappa in the **Permeability** edit field.
- 10 Click **OK**.

Boundary Conditions—Navier-Stokes Application Mode

- 1 Select **Boundary Settings** from the **Physics** menu.

2 Enter the boundary settings according to the following table:

SETTINGS	BOUNDARY 1	BOUNDARY 5,6	BOUNDARY 10	ALL OTHERS
Boundary type	Inlet	Wall	Outlet	Wall
Boundary condition	Laminar inflow	Slip	Pressure	No slip
U_0	u_{in}			
P_0			0	

3 Click **OK**.

Subdomain Settings—Convection and Diffusion

1 From the **Multiphysics** menu select **Convection and Diffusion (chcd)**.

2 From the **Physics** menu select **Subdomain Settings**.

3 From the **Subdomain selection** list, select Subdomain 2.

4 Select **reactions** from the **Group** list.

Note how the **Reaction rate** edit fields are automatically filled in as a result of exporting the group **reactions** from the Reaction Engineering Lab.

5 Select all subdomains by pressing Ctrl+A and clicking the **Subdomain selection** list.

6 On page **c_CH4** type u in the **x-velocity** edit field and v in the **y-velocity** edit field.

7 Go to page **c_H2** and type u in the **x-velocity** edit field and v in the **y-velocity** edit field.

8 Click **Apply**.

9 Click the **Init** page and type 50 in the **c_CH4(t_0)** edit field.

10 Click **Apply**.

11 Type expressions into the **Diffusion coefficient** edit field according to the following table:

SUBDOMAIN	PAGE / C_CH4	PAGE / C_H2
1	D_CH4	D_H2
2	$k_{eff} \cdot D_{CH4}$	$k_{eff} \cdot D_{H2}$
3	D_CH4	D_H2

12 Click **OK**.

Boundary Conditions—Convection and Diffusion

1 From the **Physics** menu select **Boundary Settings**.

- 2 Enter the boundary conditions for the species **c_CH4** and **c_H2** according to the following table:

SETTINGS	BOUNDARY I	BOUNDARY I0	ALL OTHER
Boundary condition	Concentration	Convective flux	Insulation/Symmetry
c_CH4 ₀	cCH4_in		
c_H2 ₀	cH2_in		

- 3 Click **OK**.

Subdomain Settings—PDE, General Form

- 1 From the **Multiphysics** menu select **PDE, General Form (g)**.
- 2 From the **Physics** menu select **Subdomain Settings**.
- 3 Select 1 and 3 in the **Subdomain selection** list and clear the **Active in this domain** check box.
- 4 Select 2 in the **Subdomain selection** list.
- 5 Type 0 in the two **Flux vector** edit fields.
- 6 Type -por*r_1_rxn_chcd/M_C/rho_soot in the **Source term** edit field.

The above settings have reduced the general form PDE

$$e_a \frac{\partial^2 \phi}{\partial t^2} + d_a \frac{\partial \phi}{\partial t} + \nabla \cdot \Gamma = F$$

to the form of the void fraction balance (Equation 4-223)

$$d_a \frac{\partial \phi}{\partial t} = F = -\frac{\varepsilon r}{M_c \rho_{\text{soot}}}$$

- 7 Go to the **Init** page.
- 8 Type por0 in the **por(t₀)** edit field.
- 9 Click **OK**.

Boundary Conditions—PDE, General Form

- 1 From the **Physics** menu select **Boundary Settings**.
- 2 Select Boundaries 4, 5, 6 and 7 and select the **Neumann boundary condition** option button.
- 3 Click **OK**.

OPTIONS AND SETTINGS

- 1 From the **Options** menu select **Constants**.
- 2 Enter the following parameter names and values in the **Constants** dialog box, either by typing them in, or by clicking the **Import Variables From File** button and browsing to the file: carbon_deposition_constants.txt, followed by clicking **Open**.

NAME	EXPRESSION	DESCRIPTION
u_in	0.667e-3	average inlet velocity
cCH4_in	50	inlet concentration
ch2_in	0	inlet concentration
kappa0	1e-9	permeability of clean catalyst
por0	0.4	porosity of clean catalyst bed
rho_soot	4e3	density of soot deposits
M_C	12.011e-3	molar weight of carbon
D_CH4	1e-6	diffusion coefficient
D_H2	4e-6	diffusion coefficient
k_eff	0.1	effectiveness factor

- 3 Click **OK**.
- 4 From the **Options** menu select **Expressions>Scalar Expressions**.
- 5 Enter the following parameter names and expressions, then click **OK**.

NAME	EXPRESSION	DESCRIPTION
kappa	kappa0*(por/por0)^3.55	permeability

MESH GENERATION

- 1 From the **Mesh** menu choose **Free Mesh Parameters**.
- 2 Click the **Boundary** tab.
- 3 Select the appropriate entries in the **Boundary selection** list and enter the following mesh settings:

BOUNDARY	MAXIMUM ELEMENT SIZE
2-9	5e-3

- 4 Click the **Remesh** button and then the **OK** button.

COMPUTING THE SOLUTION

Start by computing a flow field where chemical reactions are disregarded. This is to have a good starting guess for the flow when solving the coupled problem.

- 1 From the **Solve** menu select **Solver Parameters**.
- 2 Select **Stationary** from the **Solver** list.
- 3 Click **OK**.
- 4 From the **Solve** menu select **Solver Manager**.
- 5 On the **Solve For** page, select **Incompressible Navier-Stokes (chns)** in the **Solve for variables** tree.
- 6 Click the **OK** button.
- 7 Click the **Solve** button on the Main toolbar.

The following steps produce a plot of the flow field:

- 1 From the **Postprocessing** menu open the **Plot Parameters** dialog box.
- 2 Go to the **Surface** page.
- 3 Select **Incompressible Navier-Stokes (chns)>Velocity field** from the **Predefined quantities** list.
- 4 Go to the **Arrow** page and select the **Arrow plot** check box.
- 5 Select **Incompressible Navier-Stokes (chns)>Velocity field** from the **Predefined quantities** list.
- 6 Click **OK**.

Proceed to solve the time-dependent problem, which takes the chemical reactions and carbon deposition into account.

- 1 From the **Solve** menu select **Solver Parameters**.
- 2 Select **Time dependent** from the **Solver** list.
- 3 Type 0:100:1000 in the **Times** edit field.
- 4 Click **OK**.
- 5 From the **Solve** menu select **Solver Manager**.
- 6 On the **Initial Value** page click the **Store Solution** button.
- 7 Click the **Stored solution** option button in the **Values of variables not solved for and linearization point** area.

- 8 Return to the **Solve For** page and select **Convection and Diffusion (chcd)** and **PDE, General Form (g)** from the **Solve for variables** tree, by pressing Ctrl and clicking the entries.
- 9 Click **OK**.
- 10 Click the **Solve** button on the Main toolbar.

Plot gas phase concentrations of methane and hydrogen in the reactive bed:

- 1 From the **Postprocessing** menu open the **Cross-Section Plot Parameters** dialog box.
- 2 On the **General** page, select **1000** from the **Solutions to use** list.
- 3 Select the **Keep current plot** check box.
- 4 Go to the **Line/Extrusion** page.
- 5 Select **Convection and Diffusion (chcd)>Concentration, c_CH4** from the **Predefined quantities** list.
- 6 Enter the following parameters in the **Cross-section line data** area:

EDIT FIELD	VALUE
x0	0.4
y0	0.05
x1	0.8
y1	0.05

- 7 Click **Apply**.
- 8 Select **Convection and Diffusion (chcd)>Concentration, c_H2** from the **Predefined quantities** list.
- 9 Click **OK**.

In the last simulation of this example, look at how the flow is affected by the deposition of soot in the porous bed.

- 1 From the **Solve** menu select **Solver Manager**.
- 2 On the **Initial Value** page click the **Store Solution** button.
- 3 In the **Store Solution** window, click **OK** to store all solutions.
- 4 Click the **Stored solution** option button in the **Values of variables not solved for and linearization point** area.
- 5 Select **All** from the **Solution at time** list.

- 6 On to the **Solve For** page, select **Incompressible Navier-Stokes (chns)** in the **Solve for variables** tree.
- 7 Click **OK**.
- 8 Click the **Solve** button on the Main toolbar.

To plot the permeability in the porous bed as a function of time follow these steps:

- 1 From the **Postprocessing** menu open the **Cross-Section Plot Parameters** dialog box.
- 2 On the **General** page, press Ctrl+A and click the **Solutions to use** list.
- 3 Select **New figure** from the **Plot in** list.
- 4 Go to the **Line/Extrusion** page.
- 5 Type kappa in the **Expression** edit field.
- 6 Click **OK**.
- 7 In the **Figure** window, click the **y log** button.

Finally, plot the reactor pressure after 1000 seconds.

- 1 From the **Postprocessing** menu open the **Plot Parameters** dialog box.
- 2 Go to the **General** page and select **1000** from the **Solutions at time** list.
- 3 Clear the **Arrow** check box.
- 4 Go to the **Surface** page.
- 5 Select **Incompressible Navier-Stokes (chns)>Pressure** from the **Predefined quantities** list.
- 6 Click **OK**.

Kinetics of Pentaerythritol Production

Introduction

Pentaerythritol is an important intermediate for the production of plastics, surface coatings, paints, dyes, and explosives. In the commercial process, pentaerythritol is produced in an aqueous alkaline medium of formaldehyde and acetaldehyde. Methanol is formed as a byproduct.

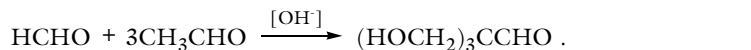
A kinetic model of a reacting system, made up of ordinary differential equations, is calibrated by finding the unknown reaction rate constants. In the present example, you fit concentration vs. time data of reacting species to a kinetic model in order to estimate the kinetic parameters.

Begin by reading the data from a text file into COMSOL Script. Based on a suggested kinetic model, evaluate rate constants and Arrhenius parameters. Then go on to simulate the kinetic model in the Reaction Engineering Lab, using the rate parameters as input. Finally, verify the kinetic model by comparing the simulation results with the experimental data, that you read into the Reaction Engineering Lab.

Reaction Kinetics

Pentaerythritol is produced through the reaction of formaldehyde and acetaldehyde with sodium hydroxide. In the batch process, the reaction temperature is typically 300 to 330 K. The product is recovered from the reaction mixture by crystallization.

Initial reactions involve rapid aldol condensations, where formaldehyde and acetaldehyde react in the presence of base, forming pentaerythritol:



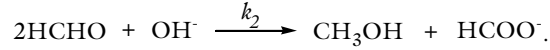
Subsequent reactions are of the Cannizarro type, in which two aldehyde molecules yield an organic acid and alcohol molecules. In the product forming step, pentaerythrose reacts with formaldehyde and base, giving pentaerythritol:

(4-226)



Two aldehyde molecules can also react with the base and form methanol as a byproduct.

(4-227)



As mentioned, the condensation reactions summarized by Equation 4-225 are comparatively fast. Consequently, by carrying out the condensation steps at low temperature, it is possible to convert acetaldehyde to pentaerythrose before any significant amount of pentaerythritol is formed. When the temperature in the reactor is raised, only the Cannizzaro reactions occur. Running a batch process in this two-step fashion makes it possible to conveniently evaluate the kinetic parameters in Equation 4-226 and Equation 4-124 (Ref. 1).

Mass Balances

Assume the Cannizzaro reactions to be of third order. Labeling HCHO as A, OH⁻ as B, and (HOCH₂)₃CCHO as C, results in the following material balances for a perfectly mixed batch reactor:

$$\frac{dc_A}{dt} = -k_1 c_A c_B c_C - 2k_2 c_A^2 c_B \quad (4-228)$$

$$\frac{dc_B}{dt} = -k_1 c_A c_B c_C - k_2 c_A^2 c_B \quad (4-229)$$

$$\frac{dc_C}{dt} = -k_1 c_A c_B c_C. \quad (4-230)$$

Written in matrix form, these equations become

$$\begin{bmatrix} \frac{dc_A}{dt} \\ \frac{dc_B}{dt} \\ \frac{dc_C}{dt} \end{bmatrix} = \begin{bmatrix} -c_A c_B c_C & -2c_A^2 c_B \\ -c_A c_B c_C & -c_A^2 c_B \\ -c_A c_B c_C & 0 \end{bmatrix} \begin{bmatrix} k_1 \\ k_2 \end{bmatrix} \quad (4-231)$$

or, equivalently,

$$\mathbf{D} = \mathbf{Mk} . \quad (4-232)$$

Evaluating Reaction Rate Parameters From Experimental Data

The following data have been measured for this reaction system at 304 K:

TABLE 4-4: EXPERIMENTAL DATA AT 304 K

TIME (S)	c_A (mol/m ³)	c_B (mol/m ³)	c_C (mol/m ³)
0	1540.20	932.00	301.80
50	1500.52	885.90	262.56
100	1454.46	856.11	232.28
150	1435.87	823.53	189.67
200	1402.37	807.21	177.64
250	1388.56	780.11	163.72
300	1368.05	771.26	152.73
350	1351.39	755.53	131.69
400	1340.76	729.96	115.52
450	1329.92	725.18	107.12
500	1314.32	711.83	112.64
550	1307.30	699.81	85.03
600	1287.82	697.17	73.89
650	1281.29	688.55	52.76
700	1282.37	678.31	60.78
750	1268.57	683.52	60.67
800	1263.14	672.27	65.68
850	1244.59	661.77	44.20
900	1245.99	661.19	44.68

TABLE 4-4: EXPERIMENTAL DATA AT 304 K

TIME (S)	c_A (mol/m ³)	c_B (mol/m ³)	c_C (mol/m ³)
950	1243.86	657.30	36.69
1000	1247.35	650.46	29.81

In this model you use a derivative approach to solve numerically for the rate constants (solve Equation 4-232). In brief, the time derivatives, \mathbf{D} , of the concentrations are determined with finite difference approximations from the experimental data in the table above. Then \mathbf{k} is solved for with a least-squares fitting procedure.

To evaluate the elements of \mathbf{D} , the three-point differentiation formulas given by Equation 4-233 to Equation 4-235 are used. In this example, Δt is constant and equal to 50 s. For each collected data-point, the formulas provide a numerical approximation to the derivatives of concentration with respect to time. For instance, for species A with concentration data recorded at constant intervals Δt from $t = 0$ to $t = m$, the derivative at the initial time is

$$\left(\frac{dc_A}{dt}\right)_{t=0} = \frac{-3c_{A(0)} + 4c_{A(1)} - c_{A(2)}}{2\Delta t} \quad (4-233)$$

and at interior times

$$\left(\frac{dc_A}{dt}\right)_{t=j} = \frac{c_{A(j+1)} - c_{A(j-1)}}{2\Delta t} \quad (4-234)$$

and at the end time

$$\left(\frac{dc_A}{dt}\right)_{t=m} = \frac{3c_{A(m-2)} - 4c_{A(m-1)} + c_{A(m)}}{2\Delta t}. \quad (4-235)$$

The matrix elements of \mathbf{M} are also calculated from the experimental data. Finally, the rate constant vector, \mathbf{k} , is solved for using the COMSOL Script function `\ (mldivide)`:

$$\mathbf{k} = \mathbf{M} \backslash \mathbf{D}. \quad (4-236)$$

The `mldivide` command performs the matrix operation $\mathbf{M}^{-1}\mathbf{M}\mathbf{k} = \mathbf{M}^{-1}\mathbf{D}$. The rate constants k_1 and k_2 are the least-square solution to the overdetermined equation system.

Determining Arrhenius Parameters

Using the procedure described above, you estimate the rate constants k_1 and k_2 at a given constant temperature. However, the values of the rate constants are dependent on the temperature, according to the Arrhenius law:

$$k_i = A_i \exp\left(\frac{-E_i}{R_g T}\right). \quad (4-237)$$

In Equation 4-237, A represents the frequency factor, E the activation energy (J/mol), R_g the ideal gas constant (J/(mol K)), and T the temperature (K). With access to experimental data at several temperatures the Arrhenius parameters, A and E can be determined.

First, for each temperature the previous procedure is applied and the rate constants are determined. Secondly, a plot of $\ln k$ vs. $1/T$ should yield a straight line, given by

$$\ln k = \ln A - \frac{E}{R_g T} \quad (4-238)$$

where the slope of the plotted line equals $-E/R_g$ and the intercept equals $\ln A$. Thus, the wanted parameters are determined by line fitting.

Experiments conducted at four different temperatures have been evaluated producing the following results for the rate constants k_1 and k_2 :

TABLE 4-5: DETERMINED VALUES FOR RATE CONSTANTS

T (K)	k_1 ($\text{m}^6/(\text{mol}^2 \cdot \text{s})$)	k_2 ($\text{m}^6/(\text{mol}^2 \cdot \text{s})$)
273	$2.7 \cdot 10^{-11}$	$7.5 \cdot 10^{-14}$
297	$7.8 \cdot 10^{-10}$	$2.2 \cdot 10^{-12}$
304	$2.1 \cdot 10^{-9}$	$5.7 \cdot 10^{-12}$
314	$6.5 \cdot 10^{-9}$	$1.8 \cdot 10^{-11}$

Results

Figure 4-103 and Figure 4-104 show the concentrations of the reactants *A* and *B* as function of time. Solid lines represent the simulated results, and symbols represent the experimental data.

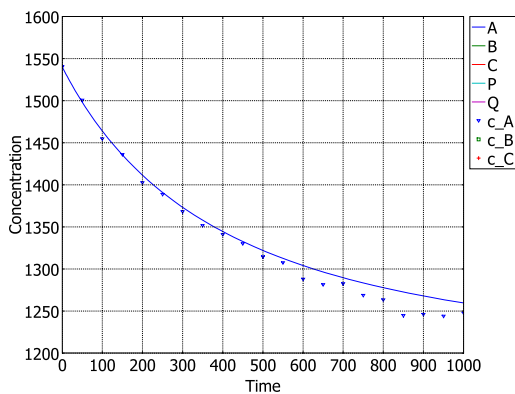


Figure 4-103: Concentration (mol/m^3) as a function of time (s) of the reactant *A*. The solid line represents simulated results while symbols represent experimental data.

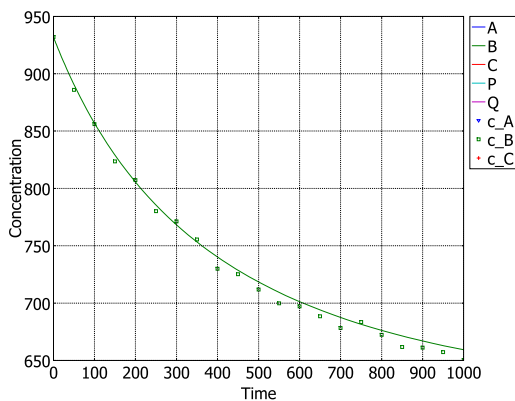


Figure 4-104: Concentration (mol/m^3) as a function of time (s) of the reactant *B*. The solid line represents simulated results while symbols represent experimental data.

Figure 4-105 shows the concentration profiles of the reactant C and also of the main product P (pentaerythritol) and byproduct Q (methanol).

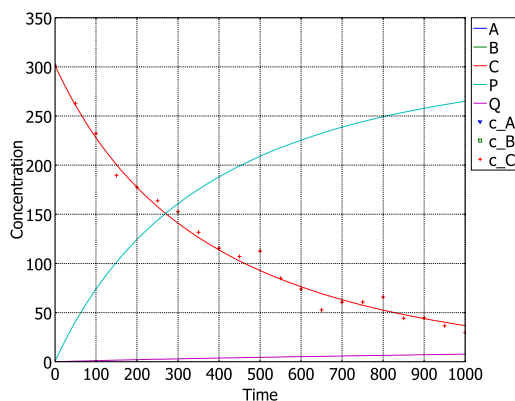


Figure 4-105: Concentration profiles (mol/m^3) as functions of time (s) of the reactant C and the products P and Q . Solid lines represent simulated results while symbols represent experimental data.

The good agreement between simulated and experimental results allows you to confirm the proposed third order kinetics of the reactions, and to determine the rate constants k_1 to $2.1 \cdot 10^{-9} \text{ (m}^6/(\text{mol}^2 \cdot \text{s}))$ and k_2 to $5.7 \cdot 10^{-12} \text{ (m}^6/(\text{mol}^2 \cdot \text{s}))$, at 304 K.

Figure 4-106 shows linear fits to experimental data, relating the rate constants k_1 (squares) and k_2 (circles) to temperature.

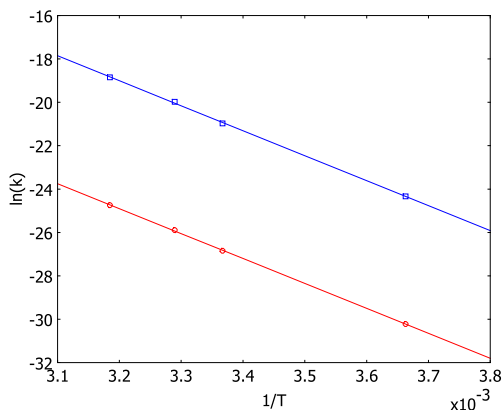


Figure 4-106: Arrhenius plots ($\ln k$ vs. $1/T$) to determine the temperature dependence of the rate constants. Solid lines represent fits to the data given by the symbols—squares for k_1 and circles for k_2 .

With reference to Equation 4-238, you readily evaluate the activation energies;

$E_1 = 95.6$ (kJ/mol) and $E_2 = 97.4$ (kJ/mol), as well as frequency factors

$A_1 = 5.364 \cdot 10^7$ ($\text{m}^6/(\text{mol}^2 \cdot \text{s})$) and $A_2 = 7.133 \cdot 10^5$ ($\text{m}^6/(\text{mol}^2 \cdot \text{s})$).

Reference

1. M.S. Peters and C.R. Cupit, *Chemical Engineering Science.*, vol. 10, p. 57, 1959.

Model Library path: Process_Chemistry/erythritol_kinetics

Modeling Using COMSOL Script

In COMSOL Script, you can estimate kinetic parameters from experimental data. You first evaluate the rate constants k_1 and k_2 by solving Equation 4-231, using data collected at 304 K. In a second step, you determine the temperature dependence of k_1 and k_2 by calculating the corresponding Arrhenius parameters.

- 1 Start **COMSOL Script**.
- 2 Move to the directory containing the text file with the experimental data:

```
cd models/Reaction_Engineering_Lab/Process_Chemistry
```

The data file `erythritol_experiments.txt` lists the experimental data of Table 4-4 in columns: the first column is the time, the following are data of concentration of the three species c_A , c_B , and c_C . The first line in the file contains the headings.

Next, you can choose between either running a ready-made script called `erythritol_kinetics_fit1.m`, which you find in the current directory, or following Instructions 3–9 below.

- 3 Create four vectors into which you read the data of the text file, skipping each column header:

```
[t Ca Cb Cc] = textread('erythritol_experiments.txt', ...  
    '%f %f %f %f', 'headerlines', 1);
```

- 4 Create a matrix of the concentration data and calculate its size:

```
C = [Ca Cb Cc];  
[m n] = size(C);
```

- 5 Define the time difference between sampling points:

```
dt = 50;
```

- 6 Make use of the three-point differentiation formulas (Equation 4-233 to Equation 4-235) and calculate the approximative time derivatives:

```
dC(1,:) = -3*C(1,:)+4*C(2,:)-C(3,:);  
dC(m,:) = 3*C(m-2,:)-4*C(m-1,:)+C(m,:);  
dC((2:(m-1)),:) = C((3:m),:)-C((1:m-2),:);
```

- 7 Set up the vector **D** of Equation 4-232:

```
D = [dC(:,1)/(2*dt); dC(:,2)/(2*dt); dC(:,3)/(2*dt)];
```

- 8 Create the matrix **M** of Equation 4-232:

```
M1 = Ca.*Cb.*Cc;  
M2 = Ca.^2.*Cb;  
z = zeros(m,1);  
M = [-M1 -2*M2; -M1 -M2; -M1 z];
```

- 9 Solve for the rate-constant vector, **k**:

```
k = M\D
```

```
k =
```

```
2.1e-009  
5.7e-012
```

You have now completed the parameter estimation of the rate constants k_1 and k_2 at 304 K. Now, move on to estimate the Arrhenius parameters for the rate constants using the data supplied in Table 4-4 and Table 4-5.

Next, you can once again choose between running a ready-made script, this time called `erythritol_kinetics_fit2.m`, or following the instructions below.

- 1 Create the following vectors with experimental values taken from Table 4-5:

```
T = [273 297 304 314];
k1 = [2.7e-11 7.8e-10 2.1e-9 6.5e-9];
k2 = [7.5e-14 2.2e-12 5.7e-12 1.8e-11];
```

- 2 Transform the data as suggested by Equation 4-238:

```
x = 1./T;
y1 = log(k1);
y2 = log(k2);
```

- 3 Fit a first-order polynomial to the transformed data:

```
p1 = polyfit(x,y1,1);
p2 = polyfit(x,y2,1);
```

- 4 Evaluate the first-order polynomials p_1 and p_2 at the points given by the vector x :

```
x_fit = 3.1e-3:1e-4:3.8e-3;
y1_fit = polyval(p1,x_fit);
y2_fit = polyval(p2,x_fit);
```

- 5 Plot the polynomials and the experimental data in the same graph and label the axes:

```
plot(x,y1,'bs',x,y2,'ro',x_fit,y1_fit,'b',x_fit,y2_fit,'r');
xlabel('1/T');ylabel('ln(k)');
```

- 6 Evaluate the Arrhenius parameters A_1 , E_1 , A_2 , and E_2 :

```
A1 = exp(p1(2))
A1 =
5.5e+007
```

```
E1 = -8.314*p1(1)
E1 =
9.6e+004
```

```
A2 = exp(p2(2))
A2 =
1.4e+005
```

```
E2 = -8.314*p2(1)
E2 =
9.6e+004
```

Modeling Using COMSOL Reaction Engineering Lab

In the Reaction Engineering Lab, set up the kinetic model of pentaerythritol production by typing the chemical reactions and rate constants into the user interface. Run the simulation and then compare the model results with experimental data directly.

In the **COMSOL Script** window, select **File>Reaction Engineering Lab**.

REACTIONS INTERFACE

- 1 From the **Model** menu, select **Reaction Settings**.
- 2 Create two entries in the **Reaction selection** list by clicking the **New** button twice.
- 3 Enter the following reaction formulas by first selecting the appropriate row in the **Reaction selection** list and then typing the text in the **Formula** edit field. Note how the Reaction Engineering Lab automatically generates reaction rate expressions and presents them in the **r** edit field.

REACTION ID #	REACTION FORMULA
1	$A+B+C \Rightarrow P$
2	$2A+B \Rightarrow Q$

- 4 Enter the values for k_1 and k_2 that you calculated previously by first selecting the appropriate row in the **Reaction selection** list and then typing the corresponding number in the **k^f** edit field:

REACTION ID #	k ^f
1	2.1×10^{-9}
2	5.7×10^{-12}

SPECIES INTERFACE

- 1 While still in the **Reaction Settings** dialog box, click the **Species** tab.
- 2 Verify that the **Species selection** list contains four species (A, B, C, P, and Q).
- 3 On the **General** page, enter the following initial concentrations in the **c₀** edit field after first having selecting the appropriate entry in the **Species selection** list:

SPECIES NAME	c ₀
A	1540
B	932
C	301.8

- 4 Click **Close**.

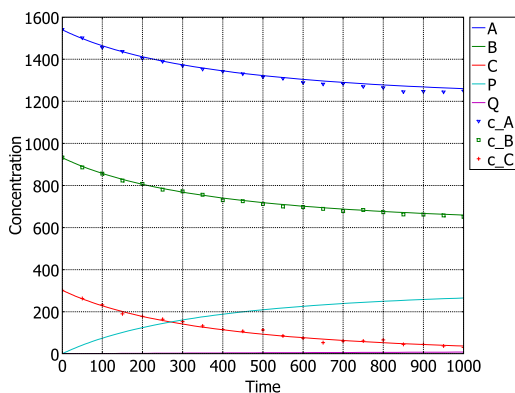
COMPUTING THE SOLUTION

- 1 Choose **Simulation>Solver Parameters**.
- 2 Clear the **Stop if steady state is reached first** check box.
- 3 In the **Times** edit field, type 1000.
- 4 Click **OK**.
- 5 Click the **Solve Problem** button (=) on the Main toolbar.

POSTPROCESSING AND VISUALIZATION

The default plot shows the time variation of the concentration of all species. For a direct comparison between the simulation results and the experiments, read the text file with experimental data into the Reaction Engineering Lab and plot it in same the graph showing the simulation results.

- 1 Choose **File>Import Experimental Data From File** to bring up the dialog for importing data from a text file.
- 2 Browse in the COMSOL installation folder to `models/Reaction_Engineering_Lab/Process_Chemistry/erythritol_experiments.txt`, and click **Import**.
- 3 Choose **Postprocessing>Plot Parameters**.
- 4 Select the **Plot experimental data** check box at the right bottom corner and click **OK** to get the following plot:



- 5 Use the zoom tools (or the **Plot Edit** dialog box) to zoom on each line in order to reproduce the figures displayed previously in the result section.

Kinetic Modeling of Cinnamaldehyde Hydrogenation

Introduction

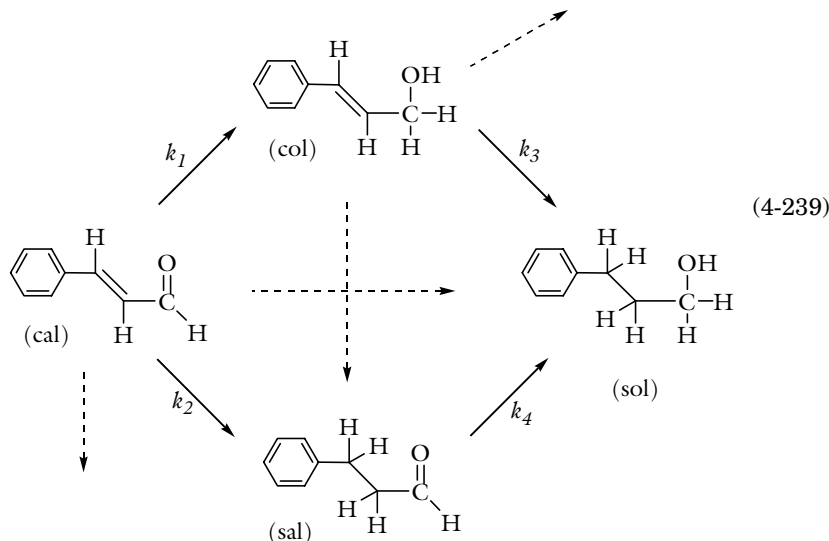
The hydrogenation of α,β -unsaturated aldehydes commonly produces a mixture of two products, namely the corresponding unsaturated alcohol as well as the saturated aldehyde. Various multi-metallic catalysts have shown promise with respect to increasing selectivity towards the desired alcohol product. In this example, the rate constants of a network of hydrogenation reactions are determined by fitting of the model parameters to experimental data. The first system under study is a binary Cu-Al catalyst and a second investigation concerns the quaternary Cu-Co-Zn-Al system.

The model illustrates the built-in parameter estimation functionality of the Reaction Engineering Lab. The reaction model is set up in the usual way, by typing chemical reaction formulas into the graphical user interface. After reading the experimental data into the software, model parameters are then estimated by means of the Gauss-Newton method.

Model Description

Exposing α,β -unsaturated cinnamaldehyde (cal) to hydrogen leads to either hydrogenation of the carbonyl to produce cinnamyl alcohol (col), or to hydrogenation of the alkene functionality to produce hydrocinnamaldehyde (sal). Further hydrogenation of both of these reaction products yields hydrocinnamyl alcohol (sol).

The corresponding reaction network is illustrated below.



Apart from the hydrogenation pathway just described, additional reactions are indicated by the dashed arrows. Cinnamaldehyde (cal) can decompose through decarbonylation and also undergo direct hydrogenation into hydrocinnamyl alcohol (sol). Cinnamyl alcohol (col) can decompose through hydrogenolysis as well as undergo isomerization to hydrocinnamaldehyde (sal). However, experiments have determined these reaction pathways to be negligible (Ref. 1), and the corresponding rate constants are not evaluated.

Experiments to evaluate catalyst performance are performed in a batch reactor autoclave, where 10 ml of cinnamaldehyde is diluted in isopropanol. 1 g of catalyst is added to the perfectly mixed system. In addition, a constant hydrogen pressure of 10 bar is applied, and the system temperature is 393 K.

Assuming that hydrogen is present in excess, the following mass balances are proposed:

$$\frac{dc_{\text{cal}}}{dt} = -k_1 c_{\text{cal}}^m - k_2 c_{\text{cal}}^n \quad (4-240)$$

$$\frac{dc_{\text{col}}}{dt} = k_1 c_{\text{cal}}^m - k_3 c_{\text{col}} \quad (4-241)$$

$$\frac{dc_{\text{sal}}}{dt} = k_2 c_{\text{cal}}^n - k_4 c_{\text{sal}} \quad (4-242)$$

$$\frac{dc_{\text{sol}}}{dt} = k_3 c_{\text{col}} + k_4 c_{\text{sal}} \quad (4-243)$$

The reaction rate constants, k_1 through k_4 , as well as the reaction orders, m and n , are to be evaluated from two sets of experiments. A first set involves a bimetallic Cu-Al catalyst while the second experiment employs a quaternary Cu-Co-Zn-Al catalyst. The concentrations of the involved species, cal, col, sal and sol are measured as a function of time, and the results are shown in Table 4-6 and Table 4-7, below.

TABLE 4-6: EXPERIMENTAL DATA FOR CU-AL CATALYST

TIME (MIN)	$c_{\text{cal}} \text{ (mol/dm}^3\text{)}$	$c_{\text{col}} \text{ (mol/dm}^3\text{)}$	$c_{\text{sal}} \text{ (mol/dm}^3\text{)}$	$c_{\text{sol}} \text{ (mol/dm}^3\text{)}$
0	0.491	0.000	0.000	0.000
15	0.486	0.006	0.008	0.000
30	0.476	0.006	0.016	0.001
45	0.460	0.018	0.024	0.001
60	0.437	0.024	0.034	0.002
90	0.407	0.034	0.049	0.005
120	0.376	0.044	0.067	0.009
150	0.347	0.051	0.083	0.013
180	0.323	0.061	0.102	0.019
210	0.294	0.068	0.119	0.025
240	0.265	0.074	0.135	0.032
270	0.233	0.078	0.149	0.039
300	0.199	0.088	0.174	0.049
330	0.171	0.088	0.180	0.054
360	0.138	0.091	0.196	0.063
390	0.108	0.099	0.220	0.074
420	0.080	0.101	0.234	0.083

TABLE 4-7: EXPERIMENTAL DATA FOR CU-CO-ZN-AL CATALYST

TIME (MIN)	$c_{\text{cal}} \text{ (mol/dm}^3\text{)}$	$c_{\text{col}} \text{ (mol/dm}^3\text{)}$	$c_{\text{sal}} \text{ (mol/dm}^3\text{)}$	$c_{\text{sol}} \text{ (mol/dm}^3\text{)}$
0	0.506	0.000	0.000	0.000
15	0.438	0.039	0.022	0.002
30	0.389	0.039	0.041	0.007
45	0.349	0.081	0.057	0.014

TABLE 4-7: EXPERIMENTAL DATA FOR CU-CO-ZN-AL CATALYST

TIME (MIN)	c_{cal} (mol/dm ³)	c_{col} (mol/dm ³)	c_{sal} (mol/dm ³)	c_{sol} (mol/dm ³)
60	0.316	0.093	0.072	0.022
90	0.258	0.101	0.095	0.040
120	0.214	0.107	0.120	0.062
150	0.179	0.104	0.139	0.084
180	0.159	0.090	0.143	0.097
210	0.135	0.084	0.158	0.118
240	0.120	0.077	0.172	0.137

Results

The first model concerns hydrogenation of cinnamaldehyde over a solid Cu-Al catalyst. Figure 4-107 shows the concentration transients of cal, col, sal, and sol (mol/dm³) evaluated from both experiments and simulation.

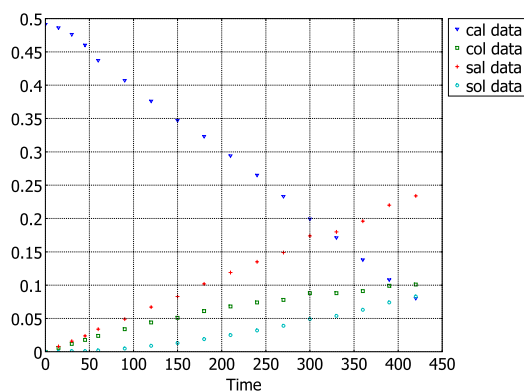


Figure 4-107: Concentration of cal, col, sal, and sol (mol/dm³) as function of time (min). Solid lines indicate simulated results while markers show experimental data. Reaction orders are $m=n=0$.

Experimental data points for the reactant aldehyde (cal) show that the concentration falls off linearly with time. This implies that the reactions depleting cal are of order zero, that is, $m = 0$ and $n = 0$. The reaction orders are held constant during the estimation of the rate constants, k_1 through k_4 . Performing parameter estimation for

different combinations of m and n , confirms that $m = 0$ and $n = 0$ gives the best model fit. Table 4-8 lists the values of rate constants and the confidence interval (95%).

TABLE 4-8: RATE CONSTANTS WHEN $M=0, N=0$

	VALUE	LOWER LIMIT	UPPER LIMIT
kf_1	4.37e-4	4.34e-4	4.40e-4
kf_2	5.61e-4	5.58e-4	5.65e-4
kf_3	3.17e-3	3.12e-3	3.21e-3
kf_4	3.00e-5	0.71e-5	5.30e-5

Figure 4-108 shows the concentration transients of cal, col, sal, and sol (mol/dm^3) evaluated for the Cu-Co-Zn-Al system.

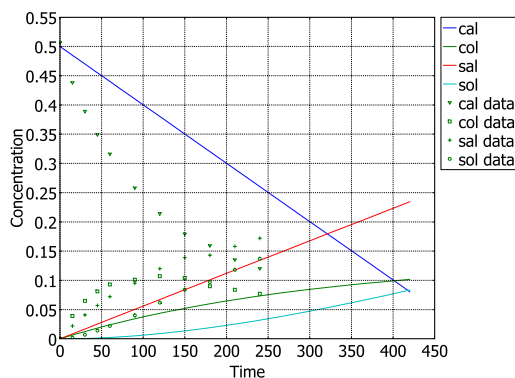


Figure 4-108: Concentration of cal, col, sal, and sol (mol/dm^3) as function of time (min). Solid lines indicate simulated results while markers show experimental data. Reaction orders are $m=2$ and $n=1$.

For the quaternary catalyst system, the aldehyde (cal) concentration falls off exponentially with time. To evaluate the proper reaction order in this case, a number of model fits are performed with m and n ranging from 1 to 2. Reaction orders $m=2$ and $n=1$ provide the best fit to data.

Table 4-9 lists the values of rate constants and the confidence interval (95%).

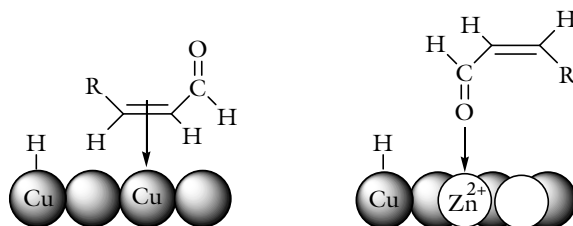
TABLE 4-9: RATE CONSTANTS WHEN $M=2, N=1$

	VALUE	LOWER LIMIT	UPPER LIMIT
kf_1	1.18e-2	1.16e-2	1.20e-2
kf_2	3.08e-3	3.04e-3	3.12e-3

TABLE 4-9: RATE CONSTANTS WHEN M=2,N=1

	VALUE	LOWER LIMIT	UPPER LIMIT
kf_3	6.04e-3	5.97e-3	6.11e-3
kf_4	4.33e-4	3.92e-4	4.73e-4

The ratio k_1/k_2 provides a measure of the selectivity of the first hydrogenation step. For the Cu-Al system, $k_1/k_2 = 0.78$, meaning that there is a preference to hydrogenate the C=C bond in cinnamaldehyde. In the case of the Cu-Co-Zn-Al system, $k_1/k_2 = 3.9$. Here, the desired hydrogenation of C=O bond is favored. The proposed explanation to this behavior is that Cu preferentially activates the alkene bond while cationic Co and Zn species activate the carbonyl (Ref. 1).



Although Cu has adverse effects with respect to selectivity, the metal is essential when it comes to producing the surface bound hydrogen needed for the hydrogenation reactions.

As can be seen from Table 4-8 and Table 4-9, the Cu-Co-Zn-Al system is considerably more active towards hydrogenation as compared to the Cu-Al catalyst. This has been correlated to the dispersion of Cu particles, which is greater in the Cu-Co-Zn-Al system. A greater dispersion means that more Cu sites are available at the catalytic surface.

Reference

1. A.J. Marchi, D.A. Gordo, A.F. Trasarti and C.R. Apesteguia, *Applied Catalysis A*, vol. 249, p. 53, 2003.

Model Library path: Process_Chemistry/cinnamaldehyde_hydrogenation

MODEL NAVIGATOR

- 1 Start the **COMSOL Reaction Engineering Lab** by double-clicking its desktop icon.
- 2 In the **Model Navigator** click the **New** button.

Start by evaluating the kinetic parameters of the Cu-Al system.

REACTIONS INTERFACE

- 1 From the **Model** menu, select **Reaction Settings**.
- 2 Create four entries in the **Reaction selection** list by clicking the **New** button four times.
- 3 Enter the reaction formulas in the table below by first selecting the appropriate row in the **Reaction selection** list and then typing the text in the corresponding **Formula** edit field.

REACTION ID #	REACTION FORMULA
1	cal=>col
2	cal=>sals
3	col=>sols
4	sals=>sols

- 4 Modify the automatically generated expressions for the reaction rates by entering the following text into the **Reaction rate** edit field.

REACTION ID #	REACTION RATE
1	kf_1*c_cal^m
2	kf_2*c_cal^n

You modify the predefined expressions by adding parameters for the reaction order. The parameters m and n will be defined later on.

- 5 Enter the following values for the **Forward rate constant** by first selecting the appropriate row in the **Reaction selection** list and then typing the corresponding number in the k^f edit field:

REACTION ID #	k^f
1	1e-3
2	1e-3
3	1e-3
4	1e-3

The values just entered for the rate constants serve as starting guesses for the parameter estimation.

SPECIES INTERFACE

- 1 While still in the **Reaction Settings** dialog box, click the **Species** tab.
- 2 Verify that the **Species selection** list contains four species (cal, col, sal, and sol).
- 3 On the **General** page, enter the following initial concentrations, one by one, in the c_0 edit field after first having selected the appropriate entry in the **Species selection** list:

SPECIES NAME	c_0
cal	0.5
col	0
sal	0
sol	0

- 4 Click **Close**.

OPTIONS AND SETTINGS

- 1 Select the menu item **Model>Constants**.
- 2 Type in the entries in the table below.

NAME	EXPRESSION	DESCRIPTION
m	0	reaction order
n	0	reaction order

- 3 Click **OK**.

Move on to load experimental data into the software and set up the parameter estimation problem.

- 1 Select the menu item **Estimation>Parameter Estimation Settings**.
- 2 On the **Data** page click the **Import From File** button.
- 3 Browse to the text file `cinnamaldehyde_hydrogenation_CuAl_data.txt` and click **Import**.
- 4 Select the entry under **Data set selection**.
- 5 Go to the **Variable Mapping** page and click through the **Data selection** list, making sure that the default association of model variables with measured variables is correct.
- 6 Click the **Parameters** page.
- 7 In the **Predefined parameters** list, select **kf_1 (Forward rate constant 1)** and then click the **>** button.
- 8 Repeat the above step for the parameters **kf_2 (Forward rate constant 2)**, **kf_3 (Forward rate constant 3)**, and **kf_4 (Forward rate constant 4)**.
- 9 Click **OK** to close the **Parameter Estimation Settings** dialog box.

COMPUTING THE SOLUTION

- 1 Click the **Estimate Parameters** button on the Main toolbar.

You find the estimated values of the rate constants and their confidence limits displayed in the **Progress - Log** window. If the **Progress - Log** window is not open, access it by following the steps below:

- 1 Select the menu item **Estimation>View Log**.
- 2 Click the **Log** page.

Note that you may have to scroll in the log to locate the summary report of the parameter estimation calculations. Selecting the **Close automatically** check box closes the **Progress - Log** window after each simulation.

You can have the software automatically update the reaction model with the new parameter values. In this example, you then find the updated values in the **Forward rate constant** edit fields, in the **Reaction Settings** dialog box. It is also your option to have the software automatically run the model simulation with the updated parameters. To set these options, follow these steps.

- 1 Select the menu item **Estimation>Parameter Estimation Settings**.
- 2 Go to the **Advanced** page.
- 3 Make sure that the check box **Copy parameter values to model after parameter estimation** is selected.

- 4 Make sure that the check box **Solve model after estimating parameters** is selected.
- 5 Click **OK**.

Now, load the data for the Cu-Co-Zn-Al system and evaluate the kinetic constants.

REACTIONS INTERFACE

- 1 Click the **Reaction Settings** button on the Main toolbar.
- 2 Make sure that the **Reactions** page is active.
- 3 Enter the following values for the **Forward rate constant** by first selecting the appropriate row in the **Reaction selection** list and then typing the corresponding number in the k^f edit field:

REACTION ID #	k^f
1	1e-3
2	1e-3
3	1e-3
4	1e-3

OPTIONS AND SETTINGS

- 1 Select the menu item **Model>Constants**.
- 2 Type in the entries in the table below; when done, click **OK**.

NAME	EXPRESSION	DESCRIPTION
m	2	reaction order
n	1	reaction order

Move on to load experimental data into the software and set up the parameter estimation problem.

- 1 Select the menu item **Estimation>Parameter Estimation Settings**.
- 2 Go to the **Data** page and click the **Import From File** button.
- 3 Browse to the text file `cinnamaldehyde_hydrogenation_CuCoZnAl_data.txt` and click **Import**.
- 4 Select **cinnamaldehyde_hydrogenation_CuAl_data.txt** from the **Data set selection** list, and deactivate the set by clearing the check box to the left of the list entry.
- 5 Select **cinnamaldehyde_hydrogenation_CuCoZnAl_data.txt** in the **Data set selection** list.

- 6 Go to the **Variable Mapping** page and click through the **Data selection** list, making sure that the default association of model variables with measured variables is correct.
- 7 Click **OK**.

COMPUTING THE SOLUTION

Click the **Estimate Parameters** button on the Main toolbar.

Chemical Vapor Deposition of GaAs

Introduction

This example illustrates the modeling of a reactor for chemical vapor deposition (CVD). In the CVD process described here, triethyl-gallium ($\text{Ga}(\text{C}_2\text{H}_5)_3$) first decomposes into a gas phase. The reaction products, along with arsine (AsH_3), then adsorb and react on a substrate to form GaAs layers. The CVD system is modeled using momentum, energy, and mass balances including a detailed description of the gas phase and adsorption kinetics (Ref. 1).

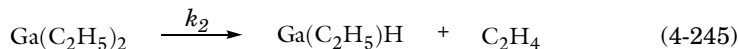
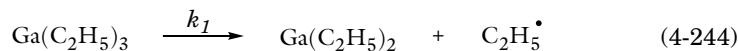
The model highlights the usability of the Reaction Engineering Lab together with the Chemical Engineering Module in COMSOL Multiphysics for simulation of complex reaction/transport systems. In the Reaction Engineering Lab you can easily study the transient behavior of different sets of reactions in a perfectly mixed system. On the basis of this analysis, you can then choose a reaction set, export it seamlessly to the Chemical Engineering Module, and investigate how the chemistry behaves in a detailed reactor geometry with surface reactions present.

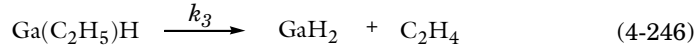
Introduction

Chemical vapor deposition is an important process for the electronics industry. A thin film is grown on a substrate by allowing molecules and molecular fragments to adsorb and react on a surface. Combining detailed chemical reaction kinetics with transport models of a CVD reactor allows for realistic modeling of the deposition process. Such simulations in turn minimize the large number of expensive and time-consuming trial runs typically required for a reactor design.

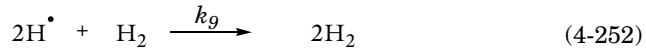
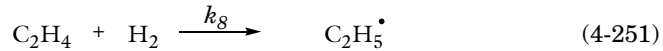
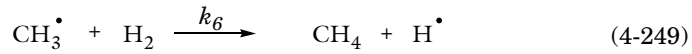
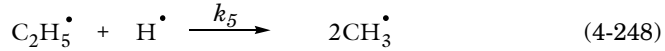
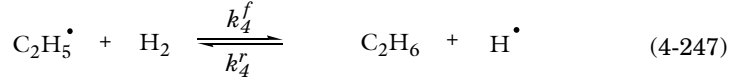
Model Definition

You can describe the gas phase decomposition of $\text{Ga}(\text{C}_2\text{H}_5)_3$ with three irreversible reactions:



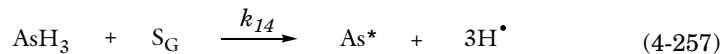
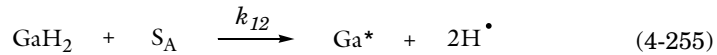
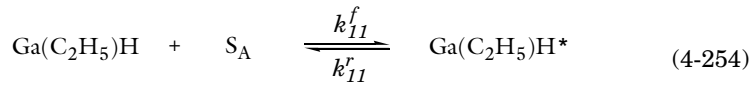


A number of radical reactions also take place in the gas phase:

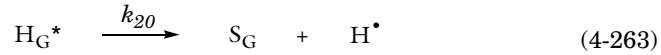
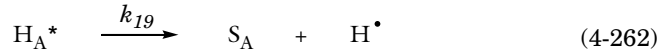
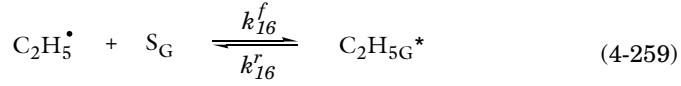
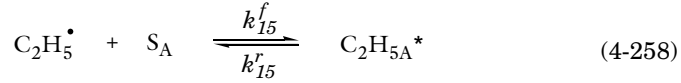


The growth of GaAs at the surface is governed by the adsorption of gas phase species and the subsequent reaction of the surface-bonded molecular fragments.

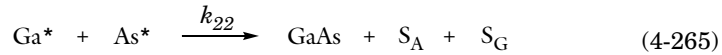
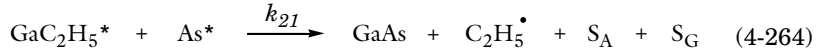
Equation 4-253 to Equation 4-257 give the surface reactions involving the Ga and As species. S_A and S_G represent surface sites, corresponding to dangling bonds of As or Ga atoms, respectively.



The surface reactions of carbon and hydrogen fragments are given by:



Finally, surface reactions leading to GaAs growth are given by:



The reaction rates ($\text{mol}/(\text{m}^3 \cdot \text{s})$) corresponding to the chemistry just described involve the mass action law

$$r_j = k_j^f \prod_{i \in \text{react}} c_i^{-\nu_{ij}} - k_j^r \prod_{i \in \text{prod}} c_i^{\nu_{ij}}. \quad (4-266)$$

Here, k_j^f and k_j^r denote the forward and reverse rate constants, respectively. The concentration of species i is denoted c_i (mol/m^3). The stoichiometric coefficients are denoted ν_{ij} , and are defined as negative for reactants and positive for products. The temperature dependence of the reaction rates is included through Arrhenius expressions for the rate constants:

$$k = AT^n \exp\left(-\frac{E}{R_g T}\right). \quad (4-267)$$

In this equation, A denotes the frequency factor, T the temperature (K), n the temperature exponent, E the activation energy (J/mol), and R_g the ideal gas constant,

8.314 J/(mol·K). The frequency factor is expressed in the units $(\text{m}^3/\text{mol})^{\alpha-1}/\text{s}$, where α is the order of the reaction.

Adsorption kinetics can also affect the overall rates. The rate of adsorption of species i at the substrate surface is

$$r_i = c_i \sqrt{\frac{R_g T}{2\pi M_i}} x_s \exp\left(-\frac{E}{R_g T}\right) \quad (4-268)$$

where c_i is the species concentration (mol/m^3), M_i denotes the molecular weight (kg/m^3), x_s is the fraction of available surface sites, and E gives the activation energy (J/mol).

In this model, the chemical species occurring in the reactions just outlined have the following labels: any label starting with SA indicates a surface species adsorbed at an arsenic site, while SG denotes a surface species adsorbed at a gallium site.

$\text{Ga}(\text{C}_2\text{H}_5)_3$	gaet3	C_2H_6	ethane
$\text{Ga}(\text{C}_2\text{H}_5)_2$	gaet2	$\text{C}_2\text{H}_5^\bullet$	et
$\text{Ga}(\text{C}_2\text{H}_5)\text{H}$	gahet	C_2H_4	ethene
GaH_2	gah2	CH_4	methane
$\text{Ga}(\text{C}_2\text{H}_5)\text{H}^*$	SAgahet	CH_3^\bullet	met
GaC_2H_5^*	SAgaet	H_2	h2
Ga^*	SAga	H^\bullet	h
AsH_3	ash3	C_2H_5^*	SAet, SGet
As^*	SGas	H^*	SAh, SGh
GaAs	gaas		

Figure 4-109: Species labels used in the model.

The analysis process follows these steps: First, take the chemistry just outlined and enter it into the Reaction Engineering Lab. Next study the material balances of different reaction networks—while assuming they are working in a perfectly mixed

batch reactor—to quickly get an overview of the reaction kinetics. Then use the Reaction Engineering Lab’s library of predefined expressions for species transport properties. With this preprocessing completed, export the reaction model to the Chemical Engineering Module to investigate the effects of the CVD reactor geometry on the reacting system. You can also study the effects of the adsorption and surface reactions.

Figure 4-110 shows the CVD reactor as drawn in COMSOL Multiphysics. The reactor is 40 cm long and 10 cm high. Located in the center is the substrate, 5 cm across and tilted 10° with respect to the vertical position. Gas enters the reactor at the inlet with a velocity of 0.4 m/s and at a pressure of 4000 Pa.

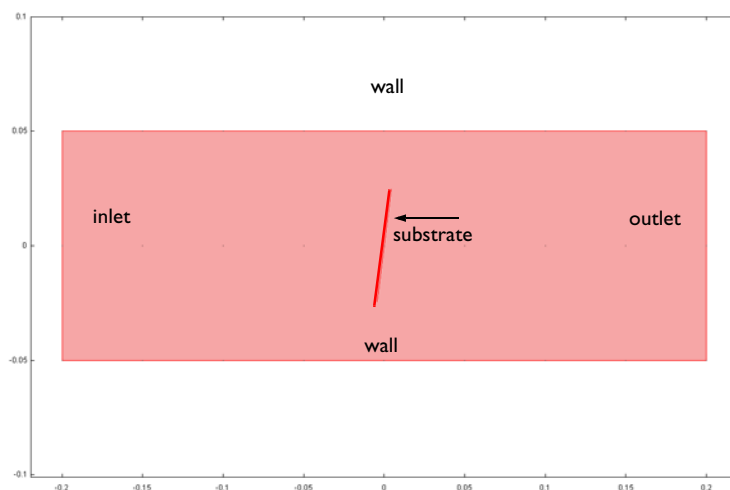


Figure 4-110: The modeling domain consists of the CVD reactor and the substrate surface.

You solve the problem in the Chemical Engineering Module using three application modes:

- Weakly Compressible Navier-Stokes
- Convection and Conduction
- Convection and Diffusion

The gas in the reactor domain is described by momentum, heat, and mass-balance equations.

The momentum balance is

$$\rho \frac{\partial \mathbf{u}}{\partial t} - \nabla \cdot \eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} + \nabla p = \mathbf{F} \quad (4-269)$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0. \quad (4-270)$$

The energy balance is

$$\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (-k \nabla T + \rho C_p T \mathbf{u}) = Q. \quad (4-271)$$

The mass balance is

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i + c_i \mathbf{u}) = R_i. \quad (4-272)$$

The boundary conditions imposed on the momentum balance are no-slip at the reactor walls and at the substrate surface, the substrate being treated as an interior boundary. Furthermore,

$$\mathbf{u} = u_0 \quad \text{inlet} \quad (4-273)$$

$$p = p_0 \quad \text{outlet} \quad (4-274)$$

$$\left[\eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2\eta}{3} (\nabla \cdot \mathbf{u}) \mathbf{I} \right] \mathbf{n} = \mathbf{0} \quad \text{outlet}. \quad (4-275)$$

The boundary conditions for the energy balance are

$$T = T_0 \quad \text{inlet} \quad (4-276)$$

$$T = T_0 \quad \text{walls} \quad (4-277)$$

$$\mathbf{n} \cdot (-k \nabla T) = 0 \quad \text{outlet}. \quad (4-278)$$

During the CVD process the substrate is heated. To model this process, impose a temperature profile at the substrate boundary:

$$T = T_{\text{surf}} \quad \text{substrate}. \quad (4-279)$$

The boundary conditions for the mass balance are insulating at the reactor walls. Furthermore,

$$c_i = c_{0,i} \quad \text{inlet} \quad (4-280)$$

$$\mathbf{n} \cdot (-D_i \nabla c_i) = 0 \quad \text{outlet} . \quad (4-281)$$

Adsorption and reaction at the substrate surface lead to a flux discontinuity given by

$$-\mathbf{n} \cdot (\mathbf{N}_1 - \mathbf{N}_2) = N_i \quad \text{substrate} \quad (4-282)$$

$$\mathbf{N}_j = -D_i \nabla c_i + c_i \mathbf{u} \quad \text{substrate} . \quad (4-283)$$

Results

As noted, the first step in the modeling process is to enter the complete set of gas phase reactions, Equation 4-244 to Equation 4-252, into the Reaction Engineering Lab for analysis. Figure 4-111 shows the species concentrations as functions of time in a perfectly mixed batch reactor kept at 900 K.

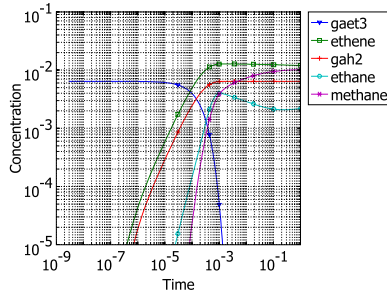


Figure 4-111: The complete set of gas phase reactions including decomposition reactions of gallium species as well as radical reactions. The chemistry occurs in a perfectly mixed batch reactor held at 900K. Radical species are not shown in the graph.

As a test, omit the radical reactions given by Equation 4-247 to Equation 4-252 from the set of gas phase reactions. Once again analyze the kinetics of the reactions describing gallium species decomposition, Equation 4-244 to Equation 4-246, at

900 K. The results appear in Figure 4-112.

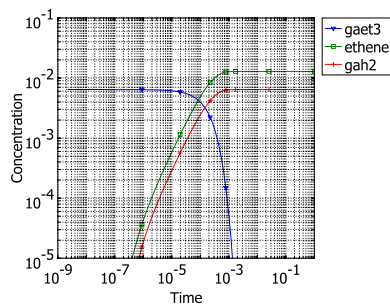


Figure 4-112: A reduced set of gas phase reactions including only the decomposition reactions of gallium species. Reactions occur in a perfectly mixed system held at 900 K.

Reducing the gas phase reaction set does not affect the reactions of the gallium species. However, excluding the radical reactions has a considerable influence on the carbon-species distribution. For the reduced reaction set, ethene and ethyl radicals are the main carbon products; for the full reaction set the main products are ethene and methane. The various species have different characteristics with respect to surface adsorption and reaction. Furthermore, the net concentration of carbon species is higher for the full reaction set. Both these factors can significantly influence the growth of surface layers. For a first study of geometrical effects on the reacting system, you can bring the reduced reaction model into the actual geometry of the CVD reactor and then solve the problem in the Chemical Engineering Module.

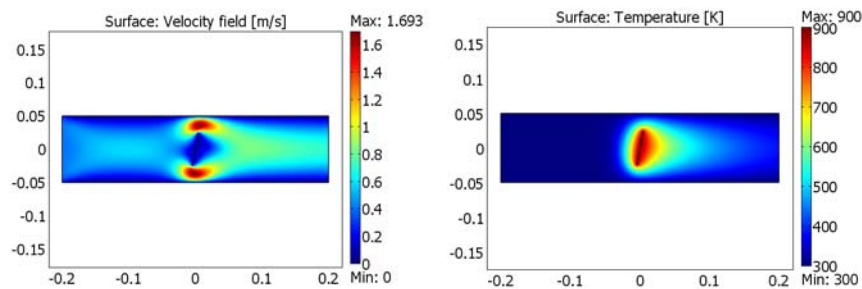


Figure 4-113: The gas phase velocity (left) and the temperature distribution (right) in the reactor domain.

Figure 4-113 shows the fluid velocity (left panel) and the temperature distribution (right panel) in the reactor domain. The gas mixture enters the reactor with a velocity

of 0.4 m/s and a temperature of 300 K with the substrate held at a constant temperature of 900 K. Notice the large effect that the heating plate has on the temperature and the expansion this causes in the fluid. This effect is seen in the average velocity, which increases downstream after the position of the substrate.

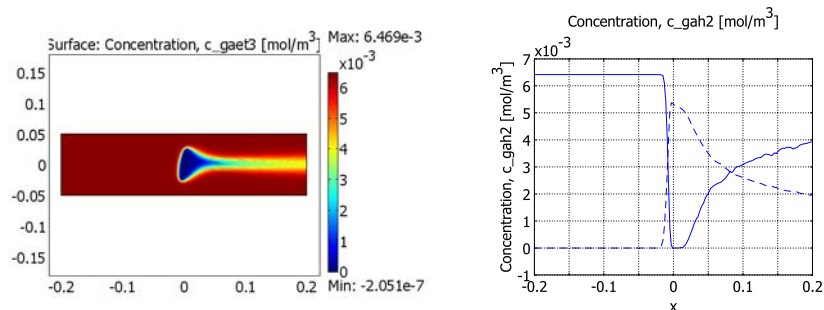


Figure 4-114: Left panel: concentration distribution of triethyl-gallium in the reactor domain. Right panel: concentration profiles of triethyl-gallium (blue line) and gallium hydride (red line) along the reactor centerline.

In Figure 4-114, the left panel shows the concentration distribution of the triethyl-gallium species in the reactor domain, while the right panel displays the concentration profile along the reactor centerline for triethyl-gallium together with that of the final product gallium hydride. Triethyl-gallium is stable at the inlet temperature (300 K) and then rapidly decomposes near the hot substrate.

Figure 4-115 shows the concentration profile of arsine along the reactor centerline. This species does not decompose in the gas phase. The decrease in concentration at the

substrate surface (at the 0 length coordinate) is due to the adsorption of arsine at the surface.

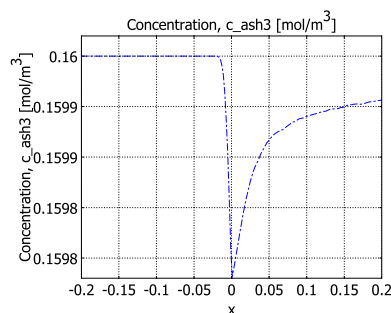


Figure 4-115: Concentration profile of arsine along the reactor centerline. Arsine is adsorbed at the substrate surface, which is located at the center of the length scale.

Figure 4-116 depicts a few of the transport properties set up in the Reaction Engineering Lab and exported to the applications modes of the COMSOL Multiphysics model. The left panel shows the diffusivities of triethyl-gallium (bottom) and arsine (top). The right panel shows the thermal conductivity of the hydrogen carrier gas. All variables are plotted as functions of temperature.

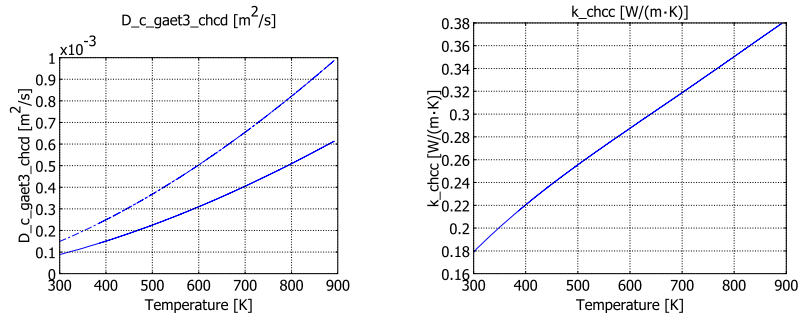


Figure 4-116: The diffusivities of triethyl-gallium (bottom) and arsine (top) as functions of temperature (left), and the thermal conductivity of the hydrogen carrier gas (right).

In summary, this model illustrates how to work with the Reaction Engineering Lab and COMSOL Multiphysics to solve an applied multiphysics problem. You set up the chemical kinetics in the Reaction Engineering Lab by entering the chemical reaction formulas. It is then easy to study different models by effortlessly activating/deactivating reactions. Then you make use of a predefined library of expressions to set up the transport properties of the reacting system before exporting the reaction model

to the Chemical Engineering Module. There you add the effect of the CVD reactor's geometry and of surface reactions to the model.

Reference

1. N.K. Ingle, C. Theodoropoulos, T.J. Mountziaris, R.M. Wexler, and F.T.J. Smith, *J. Crystal Growth*, vol. 167, p. 543, 1996.

Model Library path: Semiconductors/gaas_cvd1

Model Library path: Semiconductors/gaas_cvd2

The following path shows the location of the COMSOL Multiphysics model:

Model Library path: Reaction_Engineering_Lab/Semiconductors/gaas_cvd2

Modeling Using COMSOL Multiphysics

In this example, you first create the CVD reactor geometry in COMSOL Multiphysics and then proceed to create the reaction model in the Reaction Engineering Lab.

GEOMETRY MODELING

- 1 Open COMSOL Multiphysics and click **OK** in the **Model Navigator**.
- 2 Hold down the Shift key and click the **Rectangle/Square** button on the Draw toolbar (or choose **Draw>Specify Objects>Rectangle** from the top menu). Enter the values for the rectangle R1 given below.

EDIT FIELD	R1
width	0.4
height	0.1
position	Center

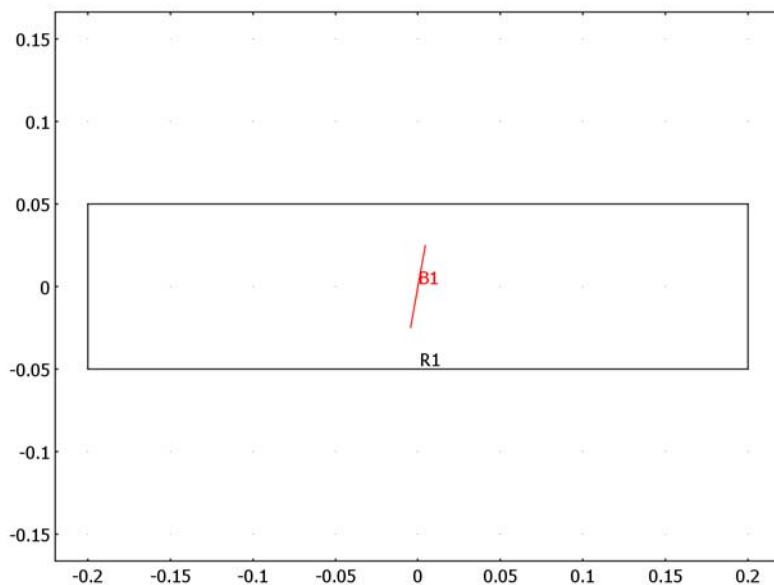
EDIT FIELD	R1
x	0
y	0

- 3 Click **OK**, then click the **Zoom Extents** button on the Main toolbar.
- 4 Hold down the Shift key and click the **Line** button on the Draw toolbar. Enter the following values for the line **B1**:

EDIT FIELD	B1
x	0 0
y	-0.025 0.025

- 5 Click **OK**.
- 6 Click the **Rotate** button on the Draw toolbar.
- 7 In the **a** edit field, type -10. Click **OK**.

The geometry should now look like the one in the picture below.



- 8 Start the Reaction Engineering Lab by choosing **File>Reaction Engineering Lab**.

Modeling Using COMSOL Reaction Engineering Lab

The model setup in the Reaction Engineering Lab consists of two parts: *gas phase reactions* and *adsorption/desorption*.

First you solve a “full” reaction model. Then you work with a reduced set of reactions, solve the model again, and compare the results. This work all takes place in the Reaction Engineering Lab. At the end of this first stage of work (outlined in the section “Gas Phase Reactions” below) you export the reaction model to COMSOL Multiphysics to the gas subdomain.

Second you set up a reaction model describing the adsorption and desorption from the surface of the substrate and export it to the substrate boundary in COMSOL Multiphysics. This takes place in the section titled “Adsorption/Desorption” on page 472.

Gas Phase Reactions

OPTIONS AND SETTINGS

- 1 Choose **Model>Model Settings** (or use the corresponding button on the Main toolbar).
- 2 Select the **Calculate thermodynamic properties** check box.
- 3 Select the **Calculate species transport properties** check box.
- 4 Type 900 in the **T** edit field.
- 5 Click **Close**.

REACTIONS INTERFACE

Start by investigating the gas phase reactions of the CVD process in the Reaction Engineering Lab modeling environment.

- 1 Choose **Model>Reaction Settings** (or click the corresponding button on the Main toolbar).
- 2 Create nine entries in the **Reaction selection** list by clicking the **New** button nine times.

- Enter the following reaction formulas by first selecting the appropriate row in the **Reaction selection** list and then entering the corresponding text in the **Formula** edit field.

REACTION ID #	REACTION FORMULA
1	gaet3=>gaet2+et
2	gaet2=>gahet+ethene
3	gahet=>gah2+ethene
4	et+h2<=>ethane+h
5	et+h=>2met
6	met+h2=>methane+h
7	2met=>ethane
8	ethene+h=>et
9	2h+h2=>2h2

- On the **Kinetics** page, specify the following Arrhenius parameters for the forward rate and reverse rate constants by first selecting the corresponding reaction number in the **Reaction selection** list, then selecting the **Use Arrhenius expressions** check box, and finally typing the corresponding numbers in the **A**, **n**, and **E** edit fields:

REACTION ID #	A forward	reverse	n forward	reverse	E forward	reverse
1	1e15		0		195e3	
2	1e18		0		195e3	
3	1e18		0		195e3	
4	3.1e-6	5.5e-4	3.6	3.5	35.6e3	21.8e3
5	3.6e7		0		0	
6	2.9e-4		3.12		36.4e3	
7	2e6		0		0	
8	1.5e2		1.49		41.8e3	
9	1e6		0		0	

SPECIES INTERFACE

- Click the **Species** tab.
- Verify that the **Species selection** list has 11 entries.
- From the **Species selection** list, select **h2**.

- 4 From the **Type** list (at the top right corner in the **Formula** area), select **Solvent**.

Note that this step automatically selects the **Lock concentration/activity** check box. This includes the influence of hydrogen concentration as a constant in the rate expressions.

- 5 For each species, specify the molecular weight and the initial concentration by first selecting the corresponding entry in the **Species selection** list and then typing the values listed in the table below in the **M** and **c₀** edit fields, respectively, both on the **General** page.

SPECIES NAME	M	c ₀
gaet3	156.7e-3	6.415e-3
gaet2	127.7e-3	0
et	29e-3	0
gahet	99.7e-3	0
ethene	28e-3	0
gah2	71.7e-3	0
h2	2e-3	1.44
ethane	30e-3	0
h	1e-3	0
met	15e-3	0
methane	16e-3	0

Molecular hydrogen is the carrier gas in the CVD process, and it is present in excess. You set hydrogen as the solvent species and assume that the hydrogen concentration is constant.

- 6 Click **Close**.

COMPUTING THE SOLUTION

- 1 Choose **Simulation>Solver Parameters**.
- 2 In the **Times** edit field, type 1.
- 3 Click **OK**.
- 4 Click the **Solve Problem** button (=) on the Main toolbar.

POSTPROCESSING AND VISUALIZATION

To produce Figure 4-111 follow these steps:

- 1 Choose **Postprocessing>Plot Parameters**.

- 2 Click the << button to clear the **Quantities to plot** list.
- 3 With the help of the Ctrl key, select the species **gaet3**, **gah2**, **ethane**, **ethene**, and **methane** from the **Predefined quantities** list.
- 4 Click the > button to add the selected species to the **Quantities to plot** list.
- 5 Click the **Line Settings** button.
- 6 From the **Line color** list, select **Cycle**.
- 7 From the **Line marker** list, select **Cycle** and then click **OK**.
- 8 From the **Plot in** list, select **New figure**.
- 9 Click **OK**.
- 10 Click the **Edit Plot** button in the toolbar of the plot window, then select the **Log scale** check box for both the **x** axis and the **y** axis.
- 11 Clear the **y-limits: Auto** check box and type $1\text{e-}5$ and $1\text{e-}1$ in the corresponding edit fields to specify the vertical plot range.
- 12 Go to the **Grid** page and clear the **Show grid** check box.
- 13 Click **OK**.

To reduce the model before simulating the process in a dimensional model, study whether it is possible to remove the non-gallium species and reactions and yet obtain approximately the same results. To do so, modify the existing reaction model by first deactivating reactions of non-gallium species. Then re-solve the material balances and compare the results with the full reaction model.

REACTIONS INTERFACE—REDUCED MODEL

- 1 Choose **Model>Reaction Settings**.
- 2 Click the **Reactions** tab.
- 3 Deactivate reactions 4 to 9 (the non-gallium reactions) by clearing the corresponding check boxes in the **Reaction selection** list.
- 4 Click **Close**.

PREPARING POSTPROCESSING—REDUCED MODEL

In order not to lose the previous plot, which is to be used for comparison, specify the location of the next plot to be a separate figure window:

- 1 Choose **Postprocessing>Plot Parameters**.
- 2 Select **New figure** in the **Plot in** list.

- 3 Click **OK**.

COMPUTING THE SOLUTION—REDUCED MODEL

Click the **Solve Problem** button on the Main toolbar.

POSTPROCESSING AND VISUALIZATION—REDUCED MODEL

- 1 Click the **Edit Plot** button in the toolbar of the new figure window, then select the **Log scale** check box for both the **x** axis and the **y** axis.
- 2 Clear the **y-limits: Auto** check box and type $1\text{e}-5$ and $1\text{e}-1$ in the corresponding edit fields to specify the vertical plot range.
- 3 Go to the **Grid** page and clear the **Show grid** check box.
- 4 Click **OK** to create Figure 4-112.

A comparison of Figure 4-111 and Figure 4-112 reveals that the gallium-related reactions remain approximately the same (see the Results section for a deeper analysis and discussion). This means that you can go on to set up a dimensional CVD model based on the reduced model instead of the one comprising all species.

In this CVD model, you add the surface adsorption/desorption kinetics to the reactions of the gas phase. Furthermore, before exporting the reduced model to the reactor geometry created in COMSOL Multiphysics, the exercise makes use of predefined expressions for species transport properties in the Reaction Engineering Lab.

Briefly summarized, the step-by-step instructions below implement the following procedure: First remove the non-gallium reactions from the reaction model. Then add the necessary data for describing the thermodynamics and transport parameters necessary for the dimensional model. Finally export the model to the reactor subdomain in COMSOL Multiphysics.

Exporting the Model to COMSOL Multiphysics

REACTIONS INTERFACE

- 1 From the **Model** menu, select **Reaction Settings**.
- 2 Click the **Reaction** tab.

- 3 Remove the non-gallium reactions by selecting each reaction in the **Reaction selection** list and clicking the **Delete** button. You end up with the following three remaining reactions:

REACTION ID #	REACTION FORMULA
1	gaet3=>gaet2+et
2	gaet2=>gahet+ethene
3	gahet=>gah2+ethene

SPECIES INTERFACE

- 1 Click the **Species** tab. You now have the following six species: **gaet3**, **gaet2**, **et**, **gahet**, **ethene**, and **gah2**; deletions from the **Reaction selection** list automatically remove the other entries from the **Species selection** list.
- 2 Add the solvent species H₂ by clicking the **New** button and entering h2 in the **Formula** edit field.
- 3 Select **Solvent** from the **Type** list next to the **Formula** edit field.
- 4 Atomic hydrogen occurs in the gas phase, and it is produced by surface reactions. Add this species by clicking the **New** button and entering h in the **Formula** edit field.
- 5 Arsine occurs in the gas phase but does not react until it adsorbs at the surface. Add this species by clicking the **New** button and entering ash3 in the **Formula** edit field.
- 6 On the **General** page—by selecting, in turn, **gaet3**, **gaet2**, **et**, **gahet**, **ethene**, and **gah2**, from the **Species selection** list—verify that the following values appear in the **Molecular weight** edit field, **M**, and the **Initial concentration** edit field, **c₀**. For the species you just added—**h2**, **h**, and **ash3**—type the values in the appropriate edit fields. Take care, in particular to select the **Lock concentration/activity** check box for the solvent species **h2**.

SPECIES NAME	M	c ₀	LOCK CONCENTRATION/ACTIVITY
gaet3	156.7e-3	6.415e-3	no
gaet2	127.7e-3	0	no
et	29e-3	0	no
gahet	99.7e-3	0	no
ethene	28e-3	0	no
gah2	71.7e-3	0	no
h2	2e-3	1.44	yes

SPECIES NAME	M	c ₀	LOCK CONCENTRATION/ACTIVITY
h	1e-3	0	no
ash3	77.9e-3	0.16	no

7 Click the **Thermo** tab.

8 Select the solvent species **h2**.

9 Type 200, 1000, and 3000 into the **T_{lower}**, **T_{midpoint}**, and **T_{upper}** edit fields, respectively.

10 Enter the following polynomial coefficients:

COMPONENT #	a _{low,k}	a _{hi,k}
1	2.3433	3.3373
2	7.9805e-3	-4.9402e-5
3	-1.9481e-5	4.9946e-7
4	2.0172e-8	-1.7957e-10
5	-7.3761e-12	2.0026e-14
6	-9.1793e2	-9.5016e2
7	6.8301e-1	-3.2050

11 Click the **Transport** tab.

12 Select the appropriate entry in the **Species selection** list and enter the following Lennard-Jones parameters (which are specific for the species and independent of the conditions) in the σ and ϵ/k edit fields:

SPECIES NAME	σ	ϵ/k
gaet3	6.245	478.6
gaet2	5.487	516.7
et	4.291	184.5
gahet	4.720	554.8
ethene	4.163	224.7
gah2	3.664	345.3
h2	2.827	59.7
h	1.825	2.31
ash3	4.145	259.8

13 Click **Close**.

EXPORT SETTINGS

- 1 Choose **File>Export>Model to COMSOL Multiphysics**.
- 2 The default choice of **Geometry** is **Geom 1 (2D)**, which is where you want to export to first. It is the gas geometry. This requires no change.
- 3 In the **Export mass balance** area, find the **Application mode** list and select **Convection and Diffusion: New**.
- 4 Type `gas_mass` in the **Group name** edit field.
- 5 In the **Export energy balance** area, find the **Application mode** list and select **Convection and Conduction: New**.
- 6 In the **Group name** edit field, type `gas_energy`.
- 7 In the **Export momentum balance** area, go to the **Application mode** list and select **Incompressible Navier-Stokes: New**.
- 8 In the **Group name** edit field, type `gas_momentum`.
- 9 Click **Export**.

Adsorption/Desorption

Now proceed to create the surface reactions that occur at the substrate. You first modify the reaction model and then export it to the substrate boundary of the 2D model. The exported reaction model describes the source terms necessary for defining the mass balance boundary conditions on the substrate surface. In this case you must first set up the surface temperature, T_{surf} , as a model parameter.

OPTIONS AND SETTINGS

- 1 Choose **Model>Model Settings**.
- 2 In the **T** edit field, type `T_surf`.
- 3 In the **p** edit field, type `p_0`.

The parameters `p_0` and `T_surf` are now defined in COMSOL Multiphysics, and these variables replace the pressure, p , and the temperature, T , respectively, in all expressions and functions.

- 4 Click **Close**.

REACTIONS INTERFACE

- 1 Click the **Reaction Settings** button.
- 2 Click the **Reactions** tab.

- 3 Deactivate the gas phase reactions by clearing all the check boxes for the reactions in the **Reaction selection** list.
- 4 Create 16 new entries in the **Reaction selection** list by clicking the **New** button repeatedly.
- 5 Type the following entries into the **Formula** edit field:

REACTION ID #	REACTION FORMULA
10	gaet3=>SAgaet+2et
11	gahet=>SAgahet
12	SAgahet=>gahet
13	gah2=>SAga+2h
14	SAgahet=>SAga+et+h
15	ash3=>SGas+3h
16	et=>SAet
17	SAet=>et
18	et=>SGet
19	SGet=>et
20	SAet=>ethene+SAh
21	SGet=>ethene+SGh
22	SAh=>h
23	SGh=>h
24	SAgaet+SGas=>gaas+et
25	SAga+SGas=>gaas

Names starting with SA refer to surface adsorbed species at arsenic sites; names starting with SG refer to surface adsorbed species at gallium sites. The notation separates the adsorption and desorption processes.

- 6 On the **Kinetics** page, enter the following Arrhenius parameters for the forward rate constants by first selecting the appropriate row in the **Reaction selection** list and then

selecting the **Use Arrhenius expressions** check box and finally entering the numbers in the **A**, **n**, and **E** edit fields:

REACTION ID #	A (forward)	n (forward)	E (forward)
10	1	0	20.9e3
11	1	0	0
12	5e8	0	146e3
13	1	0	0
14	5e11	0	134e3
15	1	0	20.9e3
16	1	0	0
17	7.9e11	0	151e3
18	1	0	0
19	7.9e11	0	151e3
20	2.5e10	0	134e3
21	2.5e10	0	134e3
22	7.2e5	0	67.4e3
23	7.2e5	0	67.4e3
24	1.1e6	0	4.18e3
25	1.1e6	0	4.18e3

For some of the adsorption reactions, the reaction rate expressions do not follow the traditional mass action law and therefore need to be modified; you set them in the form of Equation 4-268.

- 7 For each reaction in the following table, select the corresponding row in the **Reaction selection** list and replace the existing entry in the **r** edit field with the expression in the table:

REACTION ID #	r
I0	$kf_{10} \cdot c_{gaet3} \cdot (Rg \cdot T)^{0.5} / (2 \cdot \pi \cdot M_{gaet3})^{0.5} \cdot x_{A_surf}$
I1	$kf_{11} \cdot c_{gahet} \cdot (Rg \cdot T)^{0.5} / (2 \cdot \pi \cdot M_{gahet})^{0.5} \cdot x_{A_surf}$
I3	$kf_{13} \cdot c_{gah2} \cdot (Rg \cdot T)^{0.5} / (2 \cdot \pi \cdot M_{gah2})^{0.5} \cdot x_{A_surf}$
I5	$kf_{15} \cdot c_{ash3} \cdot (Rg \cdot T)^{0.5} / (2 \cdot \pi \cdot M_{ash3})^{0.5} \cdot x_{G_surf}$
I6	$kf_{16} \cdot c_{et} \cdot (Rg \cdot T)^{0.5} / (2 \cdot \pi \cdot M_{et})^{0.5} \cdot x_{A_surf}$
I8	$kf_{18} \cdot c_{et} \cdot (Rg \cdot T)^{0.5} / (2 \cdot \pi \cdot M_{et})^{0.5} \cdot x_{G_surf}$

These expressions contain the variables x_{A_surf} and x_{G_surf} , corresponding to the mole fractions of free arsenic and gallium sites, respectively. You define these variables later in COMSOL Multiphysics.

SPECIES INTERFACE

- 1 Click the **Species** tab.
- 2 Select **gaet2** from the **Species selection** list and click the check box to activate it. All 18 species present should now be active (checked) in the **Species selection** list.
- 3 Select the **Lock concentration/activity** check box for all the species below **ash3** in the **Species selection** list (that is, **SAgaet**, **SAgahet**, **SAga**, **SGas**, **SAet**, **SGet**, **SAh**, **SGh**, and **gaas**). You can do this for one species at a time or select all the species and then apply the setting.

The effect of this setting is that these species are considered to have a constant concentration in the final model, and the Reaction Engineering Lab does not create mass balance equations for them.

- 4 On the **General** page, type the following values for molecular weight and initial concentration into the **M** and **c₀** edit fields, respectively:

SPECIES NAME	M	c ₀
SAgaet	98.7e-3	1.4e-9
SAgahet	99.7e-3	0
SAga	69.7e-3	7.2e-6
SGas	74.9e-3	7.3e-6
SAet	29e-3	2.9e-8
SGet	29e-3	1.7e-8

SPECIES NAME	M	c ₀
SAh	1e-3	6.8e-8
SGh	1e-3	4e-8
gaas	144.6e-3	0

5 Click **Close**.

EXPORT SETTINGS

- 1 Select **File>Export>Model to COMSOL Multiphysics**.
- 2 From the **Domain level** list, choose **Interior boundary**.
- 3 Clear the **Export energy balance** check box; the reaction model needs only a mass balance in COMSOL Multiphysics.
- 4 In the **Export mass balance** area, go to the **Application mode** list and select **Convection and Diffusion (chcd)**.
- 5 In the **Group name** edit field, type `boundary_mass`.
- 6 Click **Export**.

Modeling Using COMSOL Multiphysics

- 1 Choose **Multiphysics>Model Navigator**.
- 2 Verify that the model contains the **Convection and Diffusion (chcd)**, **Convection and Conduction (chcc)**, and **Incompressible Navier-Stokes (chns)** application modes.
- 3 Click **OK**.

OPTIONS AND SETTINGS

- 1 Choose **Options>Constants** and define the following constants:

NAME	EXPRESSION	DESCRIPTION
u_in	0.4	Inlet velocity
T_in	300	Inlet temperature
T_surf	900	Surface temperature
p_0	4000	Outlet pressure
c_ash3_in	0.16	Inlet concentration AsH3
c_gaet3_in	6.415e-3	Inlet concentration GaEt3
x_A_surf	5e-5	Mole fraction empty A-sites
x_G_surf	2.75e-5	Mole fraction empty G-sites

2 Click **OK**.

PHYSICS SETTINGS

Subdomain Settings

- 1 Choose **Multiphysics>Convection and Diffusion (chcd)**.
- 2 Choose **Physics>Properties**.
- 3 In the dialog that appears, set **Analysis type** to **Stationary** and click **OK**.
- 4 Choose **Physics>Subdomain Settings**.
- 5 From the **Subdomain selection** list, choose **1**.
- 6 To check that the model is set up properly, verify that there are tabs with the following species names: **c_gaet3**, **c_gaet2**, **c_et**, **c_gahet**, **c_ethene**, **c_gah2**, **c_h**, and **c_ash3**.
- 7 In the **Group** list select **gas_mass**. This group was created by the export from the Reaction Engineering Lab to COMSOL Multiphysics. Note how the Reaction Engineering Lab has filled in the **D isotropic** and **R** edit fields.
- 8 For each species, type **u** in the **u** edit field and **v** in the **v** edit field. You must click on the tab for each species and repeat the setting.
- 9 Click **OK**.
- 10 Choose **Multiphysics>Convection and Conduction (chcc)**.
- 11 Choose **Physics>Properties**.
- 12 In the dialog that appears, set **Analysis type** to **Stationary** and click **OK**.
- 13 Choose **Physics>Subdomain Settings**.
- 14 In the **Group** list, select **gas_energy**. This group was created by the export from the Reaction Engineering Lab to COMSOL Multiphysics.
- 15 Type **u** in the **u** edit field and **v** in the **v** edit field.
- 16 In the **Init** tab, type T_{in} in the **T(t₀)** edit field. This sets the initial value for the temperature.
- 17 Click **OK**.
- 18 Choose **Multiphysics>Incompressible Navier-Stokes (chns)**.
- 19 Choose **Physics>Properties**.
- 20 In the dialog that appears, set **Analysis type** to **Stationary**.
- 21 Set **Weakly compressible flow** to **On** to take density variations into account properly.

22 Click **OK**.

This setting changes the name of the application to **Weakly Compressible Navier-Stokes (chns)**.

23 Choose **Physics>Subdomain Settings**.

24 In the **Subdomain selection** list, select **1**.

25 In the **Group** list, select **gas_momentum**. This group was created by the export from the Reaction Engineering Lab to COMSOL Multiphysics.

26 On the **Init** page, type p_0 in the **$p(t_0)$** edit field. This sets the initial value for the pressure.

27 Click **OK**.

Boundary Conditions

1 Choose **Multiphysics>Convection and Diffusion (chcd)**.

2 Choose **Physics>Boundary Settings**.

3 From the **Boundary selection** list, choose **1** (the inlet).

4 Specify the **Concentration** for each species by selecting this entry from the **Boundary condition** list. Do so by going through all the species tabs and setting this condition.

5 On the **c_gaet3** page, type c_{gaet3_in} in the **Concentration** edit field.

6 On the **c_ash3** page, type c_{ash3_in} in the **Concentration** edit field.

7 Select the **Interior boundaries** check box to enable interior boundary conditions.

8 Select Boundary 4 (the substrate).

9 In the **Group** list, select **boundary_mass**. This group was created by the export from the Reaction Engineering Lab to COMSOL Multiphysics. It sets the appropriate conditions for all species.

10 Select Boundary 5 (the outlet) and set **Convective flux** as the boundary condition for all species. Do so by going through all the species tabs and selecting that condition from the **Boundary conditions** list.

11 Click **OK**.

12 Choose **Multiphysics>Convection and Conduction (chcc)**.

13 Choose **Physics>Boundary Settings**.

14 Select the **Interior boundaries** check box.

15 Enter the boundary conditions in the following table:

SETTINGS	BOUNDARIES 1–3	BOUNDARY 4	BOUNDARY 5
Type	Temperature	Temperature	Convective flux
Value	T_in	T_surf	

16 Click **OK**.

17 Choose **Multiphysics>Weakly Compressible Navier-Stokes (chns)**.

18 Choose **Physics>Boundary Settings**.

19 Select the **Interior boundaries** check box.

20 Enter the boundary conditions in the following table:

SETTINGS	BOUNDARY 1	BOUNDARIES 2–4	BOUNDARY 5
Boundary type	Inlet	Wall	Outlet
Boundary condition	Velocity	No slip	Pressure, no viscous stress
u_0	u_{in}		
v_0	0		
p_0			p_0

21 Click **OK**.

MESH GENERATION

1 Choose **Mesh>Free Mesh Parameters**.

2 On the **Global** page, select **Fine** from the **Predefined mesh sizes** list.

3 On the **Boundary** page, select Boundary 4, then type $2e-3$ in the **Maximum element size** edit field.

4 Click **OK**.

COMPUTING THE SOLUTION

Now compute the solution at a substrate temperature of 900 K (which you already set in the **Constants** dialog box).

1 Click the **Solver Parameters** button.

2 Click the **Advanced** tab and clear the **Stop if error due to undefined operation** check box.

3 Click **OK**.

- 4 Choose **Solve>Solver Manager**.
- 5 On the **Solve For** page, select both **Convection and Conduction** and **Weakly Compressible Navier-Stokes**.
- 6 On the **Script** page, select the **Automatically add commands when solving** check box.
- 7 Click **Apply**, then click **Solve**. This step solves the momentum and energy balances to get a good initial value.
- 8 On the **Initial Value** page, select **Current solution** in the **Initial value** area.
- 9 On the **Solve For** page, select only **Convection and Diffusion**.
- 10 Click **Apply** and then click **Solve** to find the mass balance.
- 11 Finally, select all the application modes by clicking the **Solve For** tab and selecting the **Geom1** folder.
- 12 Click **Apply** and then click **Solve**.
- 13 Now you have the final solution. Go to the **Script** page and clear the **Automatically add commands when solving** check box. Also select the **Solve using a script** check box. These settings allow you to use the same solution technique if you wish to alter parameters in the model and solve again.
- 14 Choose **File>Save As** and type `cvd900.mph` in the edit field.

POSTPROCESSING AND VISUALIZATION

To create the left panel of Figure 4-113, follow these steps:

- 1 Choose **Postprocessing>Plot Parameters** (or use the toolbar button).
- 2 On the **Surface** page, select **Predefined quantities> Velocity field (chns)**.
- 3 Click **Apply**.
- 4 To reproduce the right panel of Figure 4-113, go to the **Surface** page. From the **Predefined quantities** list, select **Temperature (chcc)** and then click **Apply**.
- 5 To reproduce the left panel of Figure 4-114, go to the **Surface** page. From the **Predefined quantities** list, select **Concentration, c_gaet3 (chcd)**, and then click **Apply** to generate the plot.

In order to produce the remaining figures, illustrating various results along the reactor centerline, use the **Cross-Section Plot Parameters** dialog box.

- 6 Choose **Postprocessing>Cross-Section Plot Parameters**.
- 7 On the **General** page, click the **Title/Axis** button.

- 8 Select the option button next to the **Title** edit field, and type Centerline concentrations.
- 9 Select the option button next to the **Second axis label** edit field and type c_i (mol/m³).
- 10 Click **OK** to close the **Title/Axis Settings** dialog box.
- 11 On the **Line/Extrusion** page, type -0.2 and 0.2 in the **x0** and **x1** edit fields, respectively.
- 12 Select **x** in the **x-axis data** list, then click **Apply**.
- 13 From the **Predefined quantities** list, select **Concentration, c_gah2 (chcd)**.
- 14 Click the **Line Settings** button, select **Color** from the **Color** list, and click **OK**.
- 15 On the **General** page, select the **Keep current plot** check box and then click **Apply** to generate the right panel of Figure 4-114.
- 16 To generate Figure 4-115, go to the **General** page and select **Plot in: New Figure**.
- 17 Click the **Title/Axis** button, select the **Auto** buttons next to both **Title** and **Second axis label**, and click **OK**.
- 18 On the **Line/Extrusion** page, select **Concentration, c_ash3 (chcd)**.
- 19 Click the **Line Settings** button, select **Cycle** from the **Color** list, and click **OK**.
- 20 Generate the plot by clicking **Apply**.

The Reaction Engineering Lab calculates the diffusivities, the thermal conductivity, and other fluid properties, including their temperature dependence. Next, plot the diffusivities along the reactor centerline for two of the species as functions of the temperature. Again use the **Cross-Section Plot Parameters** dialog box.

- 1 On the **General** tab of the **Cross-Section Plot Parameters** dialog box, select **New figure** from the **Plot in** list.
- 2 Click the **Title/Axis** button, select the option button next to the **Title** edit field, and type Diffusion coefficients.
- 3 Select the option button next to the **Second axis label** edit field and type D_i (m²/s).
- 4 Click **OK** to close the **Title/Axis Settings** dialog box.
- 5 Click the **Line/Extrusion** tab and type $D_{c_gaet3_chcd}$ in the **Expression** edit field.
- 6 Click the bottom option button in the **x-axis data** area and then click the **Expression** button.
- 7 Type **T** in the **Expression** edit field and click **OK**.

- 8 Click **Apply** to generate the first plot.
- 9 Type `D_c_ash3_chcd` in the **Expression** edit field.
- 10 Click the **Line Settings** button, then select **Color** in the **Color** list and click **OK**.
- 11 Create the left panel of Figure 4-116 by clicking **Apply**.
Finally, plot the thermal conductivity of the hydrogen carrier gas, displayed in the right panel of Figure 4-116:
- 12 Type `k_chcc` in the **Expression** edit field.
- 13 Click the **Line Settings** button, select **Cycle** from the **Color** list, and click **OK**.
- 14 Click the **General** tab and select **New figure** from the **Plot in** list.
- 15 Click the **Title/Axis** button, select the **Auto** buttons next to both **Title** and **Second axis label**, and click **OK**.
- 16 Click **OK**.

Reference Section

Variables and Parameters in COMSOL Reaction Engineering Lab

Introduction

This section describes variables and parameters defined in COMSOL Reaction Engineering Lab. The following tables are ordered with respect to the components in the **Reaction Settings** dialog box and the **Export to COMSOL Multiphysics** dialog box.

THE REACTION KINETICS PAGE

TABLE 5-1: VARIABLES AND PARAMETERS ON THE REACTION KINETICS PAGE

PROPERTY	LABEL	EXPRESSION	NAME	SI UNIT	NOTE
k_j^f	kf_	$A^f T^{n^f} \exp\left(-\frac{E^f}{R_g T}\right)$	forward rate constant		
k_j^r	kr_	$A^r T^{n^r} \exp\left(-\frac{E^r}{R_g T}\right)$	reverse rate constant		
K_{j0}^{eq}	Keq0_	$e^{(S/R_g - H/R_g T)}$	equilibrium constant		
K_j^{eq}	Keq_	$\frac{c_m c_{n...}}{c_a c_{b...}}$	equilibrium expression		
$A_{j,j}^f, A_{j,j}^r$	Af_, Ar_	N/A	frequency factor		
$n_{j,j}^f, n_{j,j}^r$	nf_, nr_	N/A	temperature exponent		
$E_{j,j}^f, E_{j,j}^r$	Ef_, Er_	N/A	activation energy	J/(mol·K)	
r_j	r_	$r_j = k_j^f \prod c_i^{-\nu_{ij}} - k_j^r \prod c_i^{\nu_{ij}}$	reaction rate	mol/(m ³ ·s)	

THE REACTION THERMO PAGE

TABLE 5-2: VARIABLES AND PARAMETERS ON THE REACTION THERMO PAGE

PROPERTY	LABEL	EXPRESSION	NAME	SI UNIT	NOTE
H_j	H_	$H_j = \sum_i v_{ij} h_i$	enthalpy of reaction	J/mol	
S_j	S_	$S_j = \sum_i v_{ij} s_i$	entropy of reaction	J/(mol·K)	
Q_j	Q_	$Q_j = -H_j r_j$	heat source of reaction	J/(m ³ ·s)	

THE SPECIES GENERAL PAGE

TABLE 5-3: VARIABLES AND PARAMETERS ON THE SPECIES GENERAL PAGE

PROPERTY	LABEL	EXPRESSION	NAME	SI UNIT	NOTE
M_i	M_	N/A	molecular weight	kg/mol	
ρ_i	rho_	$\rho_i = \frac{p}{R_g T} M_i$	ideal gas density	kg/m ³	
ρ_i	rho_	$\rho_i = \frac{M_i}{V_{c,i} Z_i \left(1 - \frac{T}{T_{c,i}}\right)^{3/2}}$	liquid density	kg/m ³	Ref. 1
z_i	z_	N/A	charge		
$T_{c,i}$	Tc_	N/A	critical temperature	K	
$V_{c,i}$	Vc_	N/A	critical molar volume	m ³ /mol	
Z_i	Z_	N/A	compressibility factor	mol	
$c_{0,i}$	c0_	N/A	initial concentration	mol/m ³	
R_i	R_	$R_i = \sum_j v_{ij} r_j$	rate expression	mol/(m ³ ·s)	

THE SPECIES THERMO PAGE

TABLE 5-4: VARIABLES AND PARAMETERS ON THE SPECIES THERMO PAGE

PROPERTY	LABEL	EXPRESSION	NAME	SI UNIT	NOTE
h_i	h_	$h_i = R_g(a_1T + \frac{a_2}{2}T^2 + \frac{a_3}{3}T^3 + \frac{a_4}{4}T^4 + \frac{a_5}{5}T^5 + a_6)$	molar enthalpy	J/mol	gas Ref. 2
s_i	s_	$s_i = R_g(a_1 \ln T + a_2T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7)$	molar entropy	J/(mol·K)	gas Ref. 2
$C_{p,i}$	Cp_	$C_{p,i} = R_g(a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4)$	heat capacity	J/(mol·K)	gas Ref. 2
	Cp_	$C_{p,i} = R_g(a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4)$	heat capacity	J/(mol·K)	liq Ref. 10
$a_{k,1}-a_{k,7}$	aLok_ aHik_	N/A	polynomial coefficients		gas Ref. 2
$a_{k,1}-a_{k,7}$	aLok_ aHik_	N/A	polynomial coefficients		liq Ref. 10
T_{int}	Tlo_ Tmid_ Thi_	N/A	temperature interval limits	K	gas Ref. 2
T_{int}	Tlo_ Tmid_ Thi_	N/A	temperature interval limits	K	liq

THE SPECIES TRANSPORT PAGE

TABLE 5-5: VARIABLES AND PARAMETERS ON THE SPECIES TRANSPORT PAGE

PROPERTY	LABEL	EXPRESSION	NAME	UNITS	NOTE
D_i^0	D _–	$D_i^0 = 2.695 \cdot 10^{-3}$ $\cdot \frac{\sqrt{T^3 (M_i + M_0) / (2 \cdot 10^3 M_i M_0)}}{p \sigma_i \sigma_0}$ $\left(\frac{c_1}{\left(T / \sqrt{\frac{\epsilon_i}{k_B} \frac{\epsilon_0}{k_B}} \right)^{c_2}} + \frac{c_3}{e^{(c_4 T / \sqrt{\frac{\epsilon_i}{k_B} \frac{\epsilon_0}{k_B}})}} \right.$ $+ \frac{c_5}{e^{(c_6 T / \sqrt{\frac{\epsilon_i}{k_B} \frac{\epsilon_0}{k_B}})}} + \frac{c_7}{e^{(c_8 T / \sqrt{\frac{\epsilon_i}{k_B} \frac{\epsilon_0}{k_B}})}} \left. + \frac{4.748 \cdot 10^{-40} \mu_i^2 \mu_0^2}{k_B^2 T \cdot \sqrt{\frac{\epsilon_i}{k_B} \frac{\epsilon_0}{k_B}} \sigma_i^3 \sigma_0^3} \right)^{-1}$	diffusivity	m ² /s	gas Ref. 4 Ref. 5
D_i^0	D _–	$D_i^0 = \frac{3.7 \cdot 10^{-15} T \sqrt{M_0}}{\eta_0 V_{b,i}^{0.6}}$	diffusivity	m ² /s	liquid Ref. 6

TABLE 5-5: VARIABLES AND PARAMETERS ON THE SPECIES TRANSPORT PAGE

PROPERTY	LABEL	EXPRESSION	NAME	UNITS	NOTE
η_i	eta_	$\eta_i = 2.669 \cdot 10^{-6} \frac{\sqrt{T(M_i \cdot 10^3)}}{\sigma_i^2}$ $\left(\frac{b_1}{\left(T/\frac{\epsilon_i}{k_B}\right)^{b_2}} + \frac{b_3}{\exp\left(b_4 T/\frac{\epsilon_i}{k_B}\right)} + \frac{b_5}{\exp\left(b_6 T/\frac{\epsilon_i}{k_B}\right)} + \frac{4.998 \cdot 10^{-40} \mu^4}{k_B^2 T \frac{\epsilon_i}{k_B} \sigma_i^6} \right)^{-1}$	dynamic viscosity	Ns/m ²	gas Ref. 4 Ref. 5
η_i	eta_	$\eta_i = 10^{-3} ((\eta_{\text{ref}} 10^3)^{-0.2661} + \frac{T - T_{\text{ref}}}{223})^{-3.758}$	dynamic viscosity	Ns/m ²	liquid Ref. 7
k_i	k_	$k = \frac{\eta}{M} (1.15 C_p + 0.88 R_g)$	thermal conductivity	W/(m·K)	gas Ref. 8
$\eta_{i,\text{ref}}$	etaRef_	N/A	dynamic viscosity at Tref	Ns/m ²	
$T_{i,\text{ref}}$	Tref_	N/A	reference temperature	K	
$V_{b,i}$	Vb_	N/A	molar volume at boiling point	m ³ /mol	
σ_i	sigma_	N/A	characteristic length	Å	

TABLE 5-5: VARIABLES AND PARAMETERS ON THE SPECIES TRANSPORT PAGE

PROPERTY	LABEL	EXPRESSION	NAME	UNITS	NOTE
ε_i/k_b	epsilonkb_	N/A	potential energy minimum	K	
μ_i	mu_	N/A	dipole moment	D	

TABLE 5-6: VARIABLES AND PARAMETERS SET UP FOR EXPORT TO THE DIFFUSION APPLICATION MODE (CHDI)

PROPERTY	EXPRESSION	NAME	SI UNIT	NOTE
R_i	$R_i = \sum_j v_{ij} r_j$	rate expression	mol/(m ³ ·s)	
D_i^0	$D_i^0 = 2.695 \cdot 10^{-3} \cdot \frac{\sqrt{T^3(M_i + M_0)/(2 \cdot 10^3 M_i M_0)}}{p \sigma_i \sigma_0} \cdot \left(\frac{c_1}{\left(T/\sqrt{\frac{\varepsilon_i \varepsilon_0}{k_B k_B}}\right)^{c_2}} + \frac{c_3}{e^{(c_4 T/\sqrt{\frac{\varepsilon_i \varepsilon_0}{k_B k_B}})}} + \frac{c_5}{e^{(c_6 T/\sqrt{\frac{\varepsilon_i \varepsilon_0}{k_B k_B}})}} + \frac{c_7}{e^{(c_8 T/\sqrt{\frac{\varepsilon_i \varepsilon_0}{k_B k_B}})}} + \frac{4.748 \cdot 10^{-40} \mu_i^2 \mu_0^2}{k_B^2 T \cdot \sqrt{\frac{\varepsilon_i \varepsilon_0}{k_B k_B}} \sigma_i^3 \sigma_0^3} \right)^{-1}$	diffusivity	m ² /s	gas Ref. 4 Ref. 5
D_i^0	$D_i^0 = \frac{3.7 \cdot 10^{-15} T \sqrt{M_0}}{\eta_0 V_{b,i}^{0.6}}$	diffusivity	m ² /s	liquid Ref. 6
$c_{0,i}$	N/A	initial concentration	mol/m ³	

TABLE 5-7: VARIABLES AND PARAMETERS SET UP FOR EXPORT TO THE CONVECTION AND DIFFUSION APPLICATION MODE (CHCD)

PROPERTY	EXPRESSION	NAME	SI UNIT	NOTE
R_i	$R_i = \sum_j v_{ij} r_j$	rate expression	mol/(m ³ ·s)	
D_i^0	$D_i^0 = 2.695 \cdot 10^{-3}$ $\cdot \frac{\sqrt{T^3(M_i + M_0)/(2 \cdot 10^3 M_i M_0)}}{p \sigma_i \sigma_0}$ $\left(\frac{c_1}{\left(T / \sqrt{\frac{\epsilon_i}{k_B} \frac{\epsilon_0}{k_B}} \right)^{c_2}} + \frac{c_3}{e^{(c_4 T / \sqrt{\frac{\epsilon_i}{k_B} \frac{\epsilon_0}{k_B}})}} \right.$ $+ \frac{c_5}{e^{(c_6 T / \sqrt{\frac{\epsilon_i}{k_B} \frac{\epsilon_0}{k_B}})}} + \frac{c_7}{e^{(c_8 T / \sqrt{\frac{\epsilon_i}{k_B} \frac{\epsilon_0}{k_B}})}} \left. + \frac{4.748 \cdot 10^{-40} \mu_i^2 \mu_0^2}{k_B^2 T \cdot \sqrt{\frac{\epsilon_i}{k_B} \frac{\epsilon_0}{k_B}} \sigma_i^3 \sigma_0^3} \right)^{-1}$	diffusivity	m ² /s	gas Ref. 4 Ref. 5
D_i^0	$D_i^0 = \frac{3.7 \cdot 10^{-15} T \sqrt{M_0}}{\eta_0 V_{b,i}^{0.6}}$	diffusivity	m ² /s	liquid Ref. 6
$c_{0,i}$	N/A	initial concentration	mol/m ³	

TABLE 5-8: VARIABLES AND PARAMETERS SET UP FOR EXPORT TO THE MAXWELL-STEFAN DIFFUSION AND CONVECTION APPLICATION MODE (CHMS)

PROPERTY	EXPRESSION	NAME	SI UNIT	NOTE
R_i	$R_i = M_i \sum_j v_{ij} r_j$	rate expression	kg/(m ³ ·s)	
D_{AB}	$D_{AB} = 2.695 \cdot 10^{-3}$ $\cdot \frac{\sqrt{T^3 (M_i + M_0) / (2 \cdot 10^3 M_i M_0)}}{p \sigma_i \sigma_0}$ $\left(\frac{c_1}{\left(T / \sqrt{\frac{\epsilon_i \epsilon_0}{k_B k_B}} \right)^{c_2}} + \frac{c_3}{e^{(c_4 T / \sqrt{\frac{\epsilon_i \epsilon_0}{k_B k_B}})}} \right.$ $+ \frac{c_5}{e^{(c_6 T / \sqrt{\frac{\epsilon_i \epsilon_0}{k_B k_B}})}} + \frac{c_7}{e^{(c_8 T / \sqrt{\frac{\epsilon_i \epsilon_0}{k_B k_B}})}} \left. + \frac{4.748 \cdot 10^{-40} \mu_i^2 \mu_0^2}{k_B^2 T \cdot \sqrt{\frac{\epsilon_i \epsilon_0}{k_B k_B}} \sigma_i^3 \sigma_0^3} \right)^{-1}$	binary diffusion coefficients	m ² /s	gas Ref. 4 Ref. 5
ρ_{fluid}	$\rho_{\text{fluid}} = \frac{p}{R_g T} \sum_i x_{i,ms} M_i$	fluid density	kg/m ³	
p	N/A	pressure	Pa	
T	N/A	temperature	T	
M	N/A	molecular weight	kg/mol	
$w_{0,i}$	$w_{0,i} = \frac{c_{0,i} M_i}{\sum_i c_{0,i} M_i}$	initial weight fraction		

TABLE 5-9: VARIABLES AND PARAMETERS SET UP FOR EXPORT TO THE CONDUCTION APPLICATION MODE (HT)

PROPERTY	EXPRESSION	NAME	SI UNIT	NOTE
Q	$Q = \sum_j Q_j$	heat source	J/(m ³ ·s)	
$c_{p, \text{solv}}$	$c_{p, \text{solv}} = \frac{C_p}{M}$	solvent heat capacity	J/(kg·K)	export to ht with chdi, chcd
$c_{p, \text{fluid}}$	$c_{p, \text{fluid}} = \sum_i w_{i, ms} \frac{C_{p, i}}{M_i}$	fluid heat capacity	J/(kg·K)	export to ht with chms
ρ_{solv}	$\rho_{\text{solv}} = \frac{pM}{R_g T}$	solvent density	kg/m ³	gas export to ht with chdi, chcd
ρ_{solv}	$\rho_{\text{solv}} = \frac{M}{V_c Z \left(1 - \frac{T}{T_c}\right)^{\frac{2}{7}}}$	solvent density	kg/m ³	liquid Ref. I export to ht with chdi, chcd
ρ_{fluid}	$\rho_{\text{fluid}} = \frac{p}{R_g T} \sum_i x_{i, ms} M_i$	fluid density	kg/m ³	export to ht with chms
k_{solv}	$k_{\text{solv}} = \frac{\eta}{M} (1.15 C_p + 0.88 R_g)$	solvent thermal conductivity	W/(m·K)	gas Ref. II export to ht with chdi, chcd

TABLE 5-9: VARIABLES AND PARAMETERS SET UP FOR EXPORT TO THE CONDUCTION APPLICATION MODE (HT)

PROPERTY	EXPRESSION	NAME	SI UNIT	NOTE
k_{solv}	k_i	solvent thermal conductivity	W/(m·K)	
k_{fluid}	$k_{\text{fluid}} = \frac{1}{2} \left(\sum_{i=1} x_{i,ms} k_i + \left(\sum_{i=1} \frac{x_{i,ms}}{k_i} \right)^{-1} \right)$	fluid thermal conductivity	W/(m·K)	export to ht with chms Ref. 12

TABLE 5-10: VARIABLES AND PARAMETERS SET UP FOR EXPORT TO THE CONVECTION AND CONDUCTION APPLICATION MODE (CHCC)

PROPERTY	EXPRESSION	NAME	SI UNIT	NOTE
Q	$Q = \sum_j Q_j$	heat source	J/(m ³ ·s)	
$c_{p, \text{solv}}$	$c_{p, \text{solv}} = \frac{C_p}{M}$	solvent heat capacity	J/(kg·K)	export to chcc with chdi, chcd
$c_{p, \text{fluid}}$	$c_{p, \text{fluid}} = \sum_i w_{i,ms} \frac{C_{p,i}}{M_i}$	fluid heat capacity	J/(kg·K)	export to chcc with chms
ρ_{solv}	$\rho_{\text{solv}} = \frac{pM}{R_g T}$	solvent density	kg/m ³	gas export to chcc with chdi, chcd
ρ_{solv}	$\rho_{\text{solv}} = \frac{M}{V_c Z \left(1 - \frac{T}{T_c}\right)^{\frac{1}{2}}}$	solvent density	kg/m ³	liquid Ref. 1 export to chcc with chdi, chcd

TABLE 5-10: VARIABLES AND PARAMETERS SET UP FOR EXPORT TO THE CONVECTION AND CONDUCTION APPLICATION MODE (CHCC)

PROPERTY	EXPRESSION	NAME	SI UNIT	NOTE
ρ_{fluid}	$\rho_{\text{fluid}} = \frac{p}{R_g T} \sum_i x_{i,ms} M_i$	fluid density	kg/m ³	export to chcc with chms
k_{solv}	$k_{\text{solv}} = \frac{\eta}{M} (1.15 C_p + 0.88 R_g)$	solvent thermal conductivity	W/(m·K)	gas Ref. 11 export to chcc with chdi, chcd
k_{solv}	k_i	solvent thermal conductivity	W/(m·K)	
k_{fluid}	$k_{\text{fluid}} = \frac{1}{2} \left(\sum_{i=1} x_{i,ms} k_i + \left(\sum_{i=1} \frac{x_{i,ms}}{k_i} \right)^{-1} \right)$	fluid thermal conductivity	W/(m·K)	export to chcc with chms Ref. 12
h	$h = \frac{h_i}{M_i}$	species enthalpy	J/kg	

References

1. H.G. Rackett, *J. Chem. Eng. Data*, vol. 15, p. 514, 1970.
2. S. Gordon, B.J. McBride, *NASA Report SP-273*, 1971.
3. M. Zabransky, V. Ruzicka Jr., V. Majer, and E.S. Dolmaski, *J. Phys. Chem. Ref. Data, Monograph No. 6, Vol. I and II*, 1996.
4. R.S. Brokaw, *Ind. Eng. Process Design Develop.*, vol 8, p. 240, 1969.
5. P.D. Neufeld, A.R. Janzen, and R.A. Aziz, *J. Chem. Phys.*, vol. 57, p. 1100, 1972.
6. C.R. Wilke and P. Chang, *AIChE J*, vol. 1, p. 264, 1955.
7. W.R. Gambill, *Chem. Eng.*, vol. 66, p. 129, 1959.

8. L.I. Stiel and G. Thodos, *AIChE J.*, vol. 10, p. 26, 1964.
9. C.R. Wilke, *J. Chem. Phys.*, vol. 18, p. 517, 1950.
10. R.H. Perry and D.W. Green, *Perry's Chemical Engineering Handbook 7ed*, McGraw Hill, 1997.
11. A. Wassiljew, *Physik Z.*, vol. 5, p. 737, 1904.
12. Y.S. Touloukian, P.E. Liley, and S.C. Saxena, *Thermophysical Properties of Matter*, vol. 3, p. 45, IFI/Plenum, 1970.

I N D E X

- A**
 - activation energy 76
 - adsorption 347
 - application modes, in Chemical Engineering Module 137
 - Arrhenius expressions 75
 - for rate constants 455
 - Arrhenius law 35, 434
 - Arrhenius parameters 76
 - determining 35
 - estimating 434, 439
 - association factor of solvent 97
- B**
 - backward differentiation formula 103
 - batch reactor 56
 - variable volume 258
 - batch reactor (constant volume) 9, 57
 - BDF order 103
 - Belousov-Zhabotinsky reaction 289
 - bitmap graphics 144
 - Boltzmann's constant 65
- C**
 - cascade coupled reactors 139
 - catalytic combustion 205
 - Chemical Engineering Module 52
 - application modes in 137
 - chemical equilibrium 74
 - chemical vapor deposition 453
 - CHEMKIN files
 - importing 118
 - keywords 126
 - symbols and labeling 119
 - units 119
 - CHEMKIN transport data file 239
 - chlorine, neutralization of 359
 - combustion
 - catalytic 205
 - of methane 258
 - of ozone 187
 - comparison data 441
 - from experiments 155
 - importing 136
 - compression ignition
 - HCCI 258
 - COMSOL Script 29, 52, 143
 - exporting to 143
 - importing data from 135
 - Conduction and Convection application
 - mode 138
 - Conduction application mode 138
 - Conduction in Porous Media application
 - mode 138
 - constants, defining 100
 - Convection and Conduction in Porous Media application mode 138
 - Convection and Diffusion application
 - mode 83, 137
 - CSTR
 - non-isothermal 388
 - CSTR (constant volume) 59
 - CSTR reactor type 388
 - CVD 453
- D**
 - DAEs 104
 - DASPK 105
 - data files
 - format for 135
 - importing 135
 - data structures
 - importing 135
 - density 142
 - nonconstant 142
 - dependent variables, names of 140
 - derivative approach, for parameter estimation 433

- diesel filter 205
- differential-algebraic equations 104
- Diffusion application mode 83, 137
- diffusivity
 - as function of temperature 481
 - gas phase, solvent 96
 - liquid phase, solvent 97
- diffusivity matrix 188
- DNA degradation 154
- drug release 163
- E** Earth Science Module 52
- Electrokinetic Flow application mode 137
- energy balances
 - including 63
- enthalpy 80, 189
 - molar 89
 - of formation 15
 - of reaction 80
 - species 90
- entropy 16, 80, 197
 - molar 89
 - of formation 16
 - species 90
- equilibrium constant 78
- equilibrium expression 78
- equilibrium reactions 79
 - defining 11
 - export of 71
- equilibrium, elimination of 70, 79
- experimental data 155
 - importing 135
- exporting
 - domain levels for 140
 - energy balances 141
 - mass balances 140
 - momentum balances 142
 - selecting types for 143
 - simulation data 143
 - to Chemical Engineering Module 137
 - to COMSOL Script 143
 - variables 141
- expressions, creating 101
- F** Fickian diffusivity matrix 188
- food processing 312
- frequency factor 76
- G** gallium arsenide 453
- gas constant 76
- General Laminar Flow application mode 138
- Gibbs free energy 77, 80
- GRI-Mech 3.0 258
- guide, for model library 150
- H** HCCI engine 258
- heat capacity 90, 141
- heat source of reaction 81
- homogeneous catalysis 336
- I** ideal gas constant 65
- ideal gas law 85
- image export 144
- images
 - size of 144
- importing
 - CHEMKIN files 118
 - comparison data 136
 - data in structures 135
 - experimental data in files 135
 - kinetics files 119
 - thermodynamics files 129
 - transport files 133
- Incompressible Navier-Stokes application mode 138
- initial concentration 85
- integral approach, for parameter estimation 156

- interior boundaries, exporting to 140
- ions 74
- irreversible reactions 74, 76
 - defining 11
- K**
 - kinetic gas theory 96, 188
 - kinetic modeling 6
 - kinetics files
 - importing 119
 - rate expressions 121
 - third body reactions 120, 123
 - Kinetics page 75
- L**
 - labeling, of variables 82
 - labels, plotting on lines 116
 - launching Reaction Engineering Lab 50
 - least-squares fitting procedure 433
 - legends 116
 - Lennard-Jones potential 24, 95
 - line plot settings 116
 - lock concentration/activity 85
 - logarithmic plots 116
 - Lotka reaction 289
 - Lotka-Volterra reaction 289
- M**
 - mapping
 - of species concentrations 140
 - reordering species with 141
 - mass action law 75, 360
 - using for reaction rates 11
 - mass balance parameters 102
 - using stoichiometric matrix in 69
 - Maxwell-Stefan diffusion and convection
 - 83, 187
 - Maxwell-Stefan Diffusion and Convec-
 - tion application mode 97, 137
 - Maxwell-Stefan diffusivities 97
 - MEMS Module 52
 - methane combustion 258
 - Michaelis-Menten kinetics 163
 - microorganism 312
 - mixture properties 142
 - model library
 - guide for 150
 - in Model Navigator 53
 - Model MPH-files 53
 - Model Navigator 53
 - Model RXN-files 53
 - model settings 55
 - model validation 29
 - modeling
 - kinetics 6
 - of processes 6
 - strategy for 6, 8
 - using COMSOL Script 29
 - work flow for 50
 - molar enthalpy 89
 - molar entropy 89
 - multicomponent mixtures 141, 142, 143
- N**
 - NASA polynomial files 16
 - NASA polynomials 89
 - Nernst-Planck application mode 137
 - neutralization of chlorine 359
- O**
 - oscillating reactions 289
 - ozone combustion 187
- P**
 - parameter estimation 29, 106
 - derivative approach 433
 - integral approach 156
 - Parameter Estimation Settings dialog box
 - 106
 - perfectly mixed reacting system
 - isothermal 9
 - nonisothermal 15
 - pesticide transport 271
 - pharmaceuticals 336
 - plasmid DNA 154
 - plot axis settings 116

- plot parameters 115
- plot title settings 116
- plug-flow reactor 61
- predefined expressions, working with 90
- predefined quantities for plotting 115
- pressure 64
- process modeling 6
- products, stoichiometric coefficients for 80
- propylene glycol 388
- proteins, adsorption of 347
- pure gases, thermodynamic properties of 16
- Q** quantities to plot 115
- R** Rackett equation 85
 - rate expression 86
 - reactants, stoichiometric coefficients for 80
 - reacting fluid
 - gas 62
 - liquid 62
 - Reaction Engineering Lab
 - key features in 3
 - starting 50
 - reaction kinetics 9
 - reaction model 50
 - reaction order, determining 41
 - reaction rates, set using the mass action law 11
 - reaction selection list 73
 - identification number in 74
 - Reaction Settings dialog box 51
 - reaction type
 - equilibrium 78, 347
 - irreversible 76
 - reversible 76
 - reactions view 51, 73
 - Kinetics page 75
 - reaction selection list 73
 - reaction type 74
 - Thermo page 79
- reactor type
 - batch 56
 - batch (constant volume) 57
 - CSTR (constant volume) 59
 - plug-flow 61
 - semibatch 57
- reactors
 - perfectly mixed, isothermal 9
 - perfectly mixed, nonisothermal 15
 - space dependency in 23
- REL structures 143
- resolution, of images 144
- reversible reactions 74
 - defining 11
- rxn extension 50
- S** semibatch reactor 57
- simulation
 - exporting data from 143
 - until steady state 102
- slave species 71, 86
 - computing initial concentrations for 71, 104
 - selection of 69
- Solute Transport application mode 138
- solute-solvent approximation 83
- solvent density
 - gas 85
 - liquid 85
- solvent, association factor of 97
- solver parameters 102
- space-dependent reacting systems 23
- species
 - at steady state 83
 - ions 74
 - naming of 74

- reverting to predefined expressions
 - for 86
 - serving as solvent 83
 - species dipole moment 98
 - species selection list 82
 - species type
 - solvent 83
 - steady state 84
 - species view 51, 82
 - formula 73
 - General page 84
 - species selection list 82
 - species type 83
 - Thermo page 89
 - Transport page 95
 - starting Reaction Engineering Lab 50
 - steady state, stop simulation at 102
 - Stiel-Thodos equation 98
 - Stockmayer potential 95
 - stoichiometric coefficients 86
 - for reactants and products 80
 - stoichiometric matrix 69
 - strategy for modeling 6, 8
- T**
- temperature exponent 76
 - temperature intervals 18
 - temperature-dependent expressions 64
 - temperatures, ranges for 89
 - thermal conductivity 142
 - gas phase solvent 98
 - liquid phase, solvent 99
 - Thermo page 79, 89
 - thermodynamic expressions 89, 129
 - thermodynamic polynomials 89, 129
 - thermodynamic properties 80
 - calculating 63
 - thermodynamics files
 - importing 129
 - third body reactions 120, 123
 - Lindemann 125
 - SRI 126
 - Troe 125
 - time interval for plots 116
 - transport files
 - importing 133
 - Transport page 95
 - transport parameters 95
 - dipole moment 95
 - Lennard-Jones 95
 - Stockmayer 95
 - typographical conventions 3
- V**
- validation 29
 - variables
 - in export to COMSOL Multiphysics 141
 - labeling of 82, 119
 - vector graphics 144
 - viscosity 143
 - gas phase 97
 - liquid phase, solvent 98
 - void fraction 412
- W**
- Weakly Compressible Navier-Stokes application mode 138
 - exporting to 142
 - Wilke-Chang equation 97
- Z**
- zooming horizontally 117

