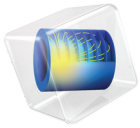


Chemical Reaction Engineering Module

User's Guide

5.6

COMSOL

Chemical Reaction Engineering Module User's Guide

© 1998–2020 COMSOL

Protected by patents listed on www.comsol.com/patents, and U.S. Patents 7,519,518; 7,596,474; 7,623,991; 8,219,373; 8,457,932; 9,098,106; 9,146,652; 9,323,503; 9,372,673; 9,454,625; 10,019,544; 10,650,177; and 10,776,541. Patents pending.

This Documentation and the Programs described herein are furnished under the COMSOL Software License Agreement (www.comsol.com/comsol-license-agreement) and may be used or copied only under the terms of the license agreement.

COMSOL, the COMSOL logo, COMSOL Multiphysics, COMSOL Desktop, COMSOL Compiler, COMSOL Server, and LiveLink are either registered trademarks or trademarks of COMSOL AB. All other trademarks are the property of their respective owners, and COMSOL AB and its subsidiaries and products are not affiliated with, endorsed by, sponsored by, or supported by those trademark owners. For a list of such trademark owners, see www.comsol.com/trademarks.

Version: COMSOL 5.6

Contact Information

Visit the Contact COMSOL page at www.comsol.com/contact to submit general inquiries, contact Technical Support, or search for an address and phone number. You can also visit the Worldwide Sales Offices page at www.comsol.com/contact/offices for address and contact information.

If you need to contact Support, an online request form is located at the COMSOL Access page at www.comsol.com/support/case. Other useful links include:

- Support Center: www.comsol.com/support
- Product Download: www.comsol.com/product-download
- Product Updates: www.comsol.com/support/updates
- COMSOL Blog: www.comsol.com/blogs
- Discussion Forum: www.comsol.com/community
- Events: www.comsol.com/events
- COMSOL Video Gallery: www.comsol.com/video
- Support Knowledge Base: www.comsol.com/support/knowledgebase

Part number: CM021601

Contents

Chapter 1: User's Guide Introduction

About the Chemical Reaction Engineering Module **14**
The Scope of the Chemical Reaction Engineering Module 14
The Chemical Reaction Engineering Module Physics Interface Guide . . . 15
The Material Database 19
Common Physics Interface and Feature Settings and Nodes 19
Where Do I Access the Documentation and Application Libraries? 19

Overview of the User's Guide **23**

Chapter 2: The Chemistry and Reaction Engineering Interfaces

Overview of the Reaction Engineering and Chemistry Interfaces **26**
Using the Reaction Node 27
Using the Species Node 30
Using the Equation View Node — Reactions and Species 32

Theory for the Reaction Engineering and Chemistry Interfaces **34**
Reaction Kinetics and Rate Expressions 34
The Equilibrium Constant 35
Handling of Equilibrium Reactions 39
Reactor Types in the Reaction Engineering Interface 42
Transport Properties 49
CHEMKIN Data and NASA Polynomials 53
Working with Predefined Expressions 54
References for the Reaction Engineering Interface 56

The Reaction Engineering Interface **57**
Features Nodes Available for the Reaction Engineering Interface 66
Initial Values 66
Reaction 67
Species 73
Reversible Reaction Group 77
Equilibrium Reaction Group. 79
Species Group 80
Additional Source 81
Reaction Thermodynamics 82
Species Activity 82
Species Thermodynamics. 82
Feed Inlet. 83
Generate Space-Dependent Model 84
Parameter Estimation 92
Experiment 93

The Chemistry Interface **96**
Feature Nodes Available for the Chemistry Interface 101
Reaction 101
Species 107
Reversible Reaction Group 110
Equilibrium Reaction Group. 112
Species Group 113
Reaction Thermodynamics 114
Species Activity 114
Species Thermodynamics. 114

Study Steps for the Reaction Engineering Interface **116**
Reactor Types and Solver Study Steps 116
Solver Study Steps for Parameter Estimation 116

Chapter 3: Chemical Species Transport Interfaces

Overview of Chemical Species Transport Interfaces **121**
Available Physics Interfaces 121

Coupling to Other Physics Interfaces 123
Adding a Chemical Species Transport Interface and Specifying the Number of Species 123

Theory for the Transport of Diluted Species Interface 126
Mass Balance Equation 127
Equilibrium Reaction Theory 128
Convective Term Formulation 130
Solving a Diffusion Equation Only 131
Mass Sources for Species Transport 131
Adding Transport Through Migration 133
Supporting Electrolytes 134
Crosswind Diffusion 135
Danckwerts Inflow Boundary Condition 136
Mass Balance Equation for Transport of Diluted Species in Porous Media 137
Convection in Porous Media 138
Diffusion in Porous Media 140
Dispersion 141
Adsorption 143
Reactions 145
Mass Transport in Fractures 146
Theory for the Reactive Pellet Bed 147
References 156

Theory for the Transport of Concentrated Species Interface 157
Multicomponent Mass Transport 157
Multicomponent Gas Diffusion: Maxwell–Stefan Description 158
Multicomponent Diffusivities 160
Multicomponent Diffusion: Mixture-Averaged Approximation 162
Multispecies Diffusion: Fick's Law Approximation 164
Multicomponent Thermal Diffusion 165
Reactive Pellet Bed 165
Regularization of Reaction Rate Expression 174
References for the Transport of Concentrated Species Interface 175

Theory for the Electrophoretic Transport Interface **176**

Theory for the Surface Reactions Interface **182**
Governing Equations for the Surface Concentrations 182
Governing Equations for the Bulk Concentrations 183
ODE Formulations for Surface Concentrations 185
Surface Reaction Equations on Deforming Geometries 186
Reference for the Surface Reactions Interface 187

Theory for the Nernst–Planck Equations Interface **188**
Governing Equations for the Nernst–Planck Formulation. 188
Convective Term Formulation. 190

Theory for the Reacting Laminar Flow Interface **191**
Pseudo Time Stepping for Mass Transport 191
The Stefan Velocity 191
The Chemical Reaction Rate 193

The Transport of Diluted Species Interface **195**
The Transport of Diluted Species in Porous Media Interface 199
Domain, Boundary, and Pair Nodes for the Transport of Diluted Species Interface. 200
Transport Properties 202
Turbulent Mixing. 204
Initial Values 205
Mass-Based Concentrations. 205
Reactions. 205
No Flux 207
Inflow 208
Outflow 208
Concentration. 209
Flux. 209
Symmetry 210
Flux Discontinuity 211
Partition Condition 211
Periodic Condition 212
Line Mass Source. 213
Point Mass Source 213

Open Boundary 214
Thin Diffusion Barrier 214
Thin Impermeable Barrier 215
Equilibrium Reaction 215
Surface Reactions 216
Surface Equilibrium Reaction 217
Fast Irreversible Surface Reaction 217
Porous Electrode Coupling 217
Reaction Coefficients 218
Electrode Surface Coupling 218
Porous Medium 219
Fluid 219
Porous Matrix 221
Dispersion 222
Unsaturated Porous Medium 222
Liquid 223
Gas 225
Adsorption 226
Volatilization 228
Reactive Pellet Bed 228
Porous Media Diffusion 231
Reactions (Reactive Pellet Bed) 231
Species Source. 233
Hygroscopic Swelling 233
Fracture 234

The Transport of Diluted Species in Fractures Interface 236
Boundary, Edge, Point, and Pair Nodes for the Transport of Diluted Species in Fractures Interface 238
Adsorption 239
Concentration 240
Flux 241
Fracture 241
Inflow 242
No Flux 243
Outflow 243
Reactions. 243
Species Source. 244

The Transport of Concentrated Species Interface **245**
Domain, Boundary, and Pair Nodes for the Transport of Concentrated Species Interface . . . 251
Transport Properties . . . 252
Porous Media Transport Properties . . . 256
Reactive Pellet Bed . . . 259
Pellet Transport Properties . . . 261
Reaction Sources (Reactive Pellet Bed) . . . 262
Electrode Surface Coupling . . . 263
Turbulent Mixing . . . 264
Reaction . . . 265
Reaction Sources . . . 266
Initial Values . . . 267
Mass Fraction . . . 268
Flux . . . 269
Inflow . . . 270
No Flux . . . 271
Outflow . . . 271
Symmetry . . . 272
Flux Discontinuity . . . 272
Open Boundary . . . 272
Equilibrium Reaction . . . 273
Surface Equilibrium Reaction . . . 274

The Nernst–Planck Equations Interface **275**
Domain and Boundary Nodes for the Nernst–Planck Equations Interface . . . 278
Convection, Diffusion, and Migration . . . 279
Electric Insulation . . . 281
No Flux . . . 281
Initial Values . . . 281
Reactions . . . 282
Concentration . . . 282
Flux . . . 283
Symmetry . . . 283
Inflow . . . 284
Outflow . . . 284
Flux Discontinuity . . . 285

Current Density 285
Current Discontinuity 286
Open Boundary 286
Reference for the Nernst–Planck Equations Interface 287

The Nernst–Planck-Poisson Equations Interface 288

The Electrophoretic Transport Interface 289
Common Settings for the Species Nodes in the Electrophoretic Transport Interface 293
Diffusion and Migration Settings 294
Domain, Boundary, and Pair Nodes for the Electrophoretic Transport Interface 295
Solvent 296
Porous Matrix Properties 296
Fully Dissociated Species 297
Uncharged Species 297
Weak Acid 297
Weak Base 297
Ampholyte 298
Protein 298
Current Source 298
Initial Potential 298
Current 299
Current Density 299
Insulation 299
Potential 299
Species Source 300
Initial Concentration 300
Concentration 300
No Flux 301
Flux 301
Inflow 301
Outflow 302

The Surface Reactions Interface 303
Boundary, Edge, Point, and Pair Nodes for the Surface Reactions Interface 304

Surface Properties 305
Initial Values 306
Reactions 306
Surface Concentration 307

The Reacting Flow Multiphysics Interface **308**
The Reacting Laminar Flow Interface 308
The Reacting Flow Coupling Feature 309
Physics Interface Features 311

The Reacting Flow in Porous Media Multiphysics Interface **313**
The Reacting Flow in Porous Media, Transport of Diluted Species Interface 313
The Reacting Flow in Porous Media, Transport of Concentrated Species Interface 314
The Reacting Flow, Diluted Species Coupling Feature 314
The Reacting Flow Coupling Feature 315
Physics Interface Features 315

Chapter 4: Fluid Flow Interfaces

Modeling Fluid Flow **318**
Available Physics Interfaces 318
Coupling to Other Physics Interfaces 319

Chapter 5: Heat Transfer Interfaces

Modeling Heat Transfer **322**
Available Physics Interfaces 322
Coupling Heat Transfer with Other Physics Interfaces 322

Chapter 6: Thermodynamics

Using Thermodynamic Properties **324**
Workflow for Thermodynamics Property Calculations 324
Thermodynamics 326
Thermodynamic System 327
External Thermodynamic Packages 335
External Thermodynamic System 336
Predefined System 339
Exporting and Importing Thermodynamic Systems 342
Species Property 342
Mixture Property 348
Equilibrium Calculation 349
Generate Chemistry 353
Generate Material 355
Coupling with the Reaction Engineering and the Chemistry Interfaces . . 359
Evaluating a Property Function in a Physics Interface 363
User-Defined Species 364
References 370

Thermodynamic Models and Theory **371**
Introduction 371
Thermodynamic Models 371
Selecting the Right Thermodynamic Model 386
Species Property References 388
Thermodynamic Properties Definitions 389
Standard Enthalpy of Formation and Absolute Entropy Terms 393
Reference State 394
Transport Properties 394
Surface Tension 419
References 420

Chapter 7: Glossary

Glossary of Terms **428**

1

User's Guide Introduction

This guide describes the Chemical Reaction Engineering Module, an optional package that extends the COMSOL Multiphysics® modeling environment with customized physics interfaces and functionality for the analysis of mass transport, chemical reactions, thermodynamic properties, and other features that are important for chemical engineering simulation.

This chapter introduces you to the capabilities of the module. A summary of the physics interfaces and where you can find documentation and model examples is also included. The last section is a brief overview with links to each chapter in this guide.

- About the Chemical Reaction Engineering Module
- Overview of the User's Guide

About the Chemical Reaction Engineering Module

In this section:

- The Scope of the Chemical Reaction Engineering Module
- The Chemical Reaction Engineering Module Physics Interface Guide
- Common Physics Interface and Feature Settings and Nodes
- The Material Database
- Where Do I Access the Documentation and Application Libraries?

The Scope of the Chemical Reaction Engineering Module

The Chemical Reaction Engineering Module is tailor-made for the modeling of chemical systems primarily affected by chemical composition, reaction kinetics, fluid flow, and temperature as functions of space, time, and each other. It has a number of physics interfaces to model chemical reaction kinetics, mass transport in dilute, concentrated, and electric potential-affected solutions, laminar and porous media flows, and energy transport.

Included in these physics interfaces are the kinetic expressions for the reacting systems and models for the definition of mass transport. A variety of ready-made expressions are also accessible in order to calculate a system's thermodynamic and transport properties.

Like all COMSOL modules, the physics interfaces described in this guide include all the steps available for the modeling process, which are described in detail in the *COMSOL Multiphysics Reference Manual* (see Where Do I Access the Documentation and Application Libraries?), for example:

- *Definitions* of parameters and model variables.
- Creating, importing, and manipulating a *geometry*.
- Specifying the chemical and transport *material properties*.
- Defining the reaction formulas and *physics* in the system and on boundaries, and coupling them to other features.

- *Meshing* a modeling domain with appropriate consideration given to the reaction system's behavior.
- Solving the equations that describe a system for stationary or dynamic behavior, or as a parametric or optimization *study*.
- Analyzing *results* to present for further use.

Once a model is defined, you can go back and make changes to all the branches listed above, while maintaining consistency in the other definitions throughout. You can restart the solver, for example, using the existing solution as an initial guess or even alter the geometry, while the equations and boundary conditions are kept consistent through the associative geometry feature. It is also useful to review the *Introduction to the Chemical Reaction Engineering Module* included with the module's documentation.

While a major focus of this module is on chemical reactors and reacting systems, it is also extensively used for systems where mass transport is the major component. This includes unit operations equipment, separation and mixing processes, corrosion, chromatography, and electrophoresis. The module is also widely used for educational purposes including courses about chemical engineering, chemical reaction engineering, electrochemical engineering, biotechnology, and transport phenomena.

In addition to its application in traditional chemical industries, it is a popular tool for investigating clean technology processes (for example, catalytic monoliths and reactive filters), applications such as microlaboratories in biotechnology, and in the development of sensors and equipment in analytical chemistry.

The notations and structure in this module were inspired by the book *Transport Phenomena* by Bird, Stewart, and Lightfoot. The work by H. Scott Fogler, *Elements of Chemical Reaction Engineering*, was also used as an inspiration.

The Chemical Reaction Engineering Module Physics Interface Guide

The appropriate physics interface for modeling a system is first chosen from the *Model Wizard*. The branches are visible (AC/DC, Acoustics, Structural Mechanics, and Mathematics) as well as the core physics interfaces (Electrostatics, for example) included with COMSOL Multiphysics. The Heat Transfer in Fluids, Single-Phase Flow, Laminar Flow, and Transport of Diluted Species interfaces are also included in

the base package but have increased functionality with this module. See the *COMSOL Multiphysics Reference Manual* for details pertaining to the base package.

- Modeling Fluid Flow
- Modeling Heat Transfer
- Creating a New Model in the *COMSOL Multiphysics Reference Manual*

When one or several physics interfaces are chosen from the **Model Wizard** (or if you open the **Add Study** window), you select an analysis type (stationary, dynamic, or parametric) and then the modeling interfaces are available as a nodes in the **Model Builder** along with all the other nodes required for modeling (Definitions, Geometry, and so forth).

By adding another physics interface, you can account for a phenomenon not previously described in a model. To do this, right-click a **Component** node in the **Model Builder** to open the **Add Physics** window. You can do this at any stage during the modeling process. This action still retains the existing geometry, equations, boundary conditions, and current solution, which you can build upon for further development of the model.

The table below lists all the physics interfaces specifically available or enhanced with this module (in addition to the basic COMSOL Multiphysics license). These physics interfaces form the backbone of the module and are based on the equations for chemical reaction kinetics, chemical species transport, as well as for fluid flow and heat transfer in porous media fundamentals.

In the *COMSOL Multiphysics Reference Manual:*

- Studies and Solvers
- The Physics Interfaces
- For a list of all the core physics interfaces included with a COMSOL Multiphysics license, see Physics Interface Guide.

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
Chemical Species Transport				
Surface Reactions		sr	all dimensions	stationary (3D, 2D, and 2D axisymmetric models only); time dependent
Transport of Diluted Species[1]		tds	all dimensions	stationary; time dependent
Transport of Diluted Species in Porous Media		tds	all dimensions	stationary; time dependent
Transport of Diluted Species in Fractures		dsf	3D, 2D, 2D axisymmetric	stationary; time dependent
Electrophoretic Transport		el	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization
Chemistry		chem	all dimensions	stationary; time dependent
Transport of Concentrated Species		tcs	all dimensions	stationary; time dependent
Nernst-Planck Equations		npe	all dimensions	stationary; time dependent
Nernst-Planck-Poisson Equations		tds+es	all dimensions	stationary; time dependent; stationary source sweep; small-signal analysis, frequency domain
Reaction Engineering		re	0D	time dependent; stationary plug flow
Reacting Flow				
Laminar Flow		—	3D, 2D, 2D axisymmetric	stationary; time dependent
Laminar Flow, Diluted Species[1]		—	3D, 2D, 2D axisymmetric	stationary; time dependent

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
Reacting Flow in Porous Media				
Transport of Diluted Species		rfds	3D, 2D, 2D axisymmetric	stationary; time dependent
Transport of Concentrated Species		rfcs	3D, 2D, 2D axisymmetric	stationary; time dependent
Fluid Flow				
Single-Phase Flow				
Creeping Flow		spf	3D, 2D, 2D axisymmetric	stationary; time dependent
Laminar Flow[1]		spf	3D, 2D, 2D axisymmetric	stationary; time dependent
Porous Media and Subsurface Flow				
Brinkman Equations		br	3D, 2D, 2D axisymmetric	stationary; time dependent
Darcy's Law		dl	all dimensions	stationary; time dependent
Free and Porous Media Flow		fp	3D, 2D, 2D axisymmetric	stationary; time dependent
Heat Transfer				
Heat Transfer in Fluids[1]		ht	all dimensions	stationary; time dependent
Heat Transfer in Solids and Fluids[1]		ht	all dimensions	stationary; time dependent
Heat Transfer in Porous Media		ht	all dimensions	stationary; time dependent

[1] This physics interface is included with the core COMSOL package but has added functionality for this module.

The Material Database

The Chemical Reaction Engineering Module includes an additional **Liquids and Gases** material database with temperature-dependent fluid dynamic and thermal properties.

- Liquids and Gases Materials Library
- Materials

Common Physics Interface and Feature Settings and Nodes

There are several common settings and sections available for the physics interfaces and feature nodes. Some of these sections also have similar settings or are implemented in the same way no matter the physics interface or feature being used. There are also some physics feature nodes that display in COMSOL Multiphysics.

In each module's documentation, only unique or extra information is included; standard information and procedures are centralized in the *COMSOL Multiphysics Reference Manual*.

In the *COMSOL Multiphysics Reference Manual* see Table 2-4 for links to common sections and Table 2-5 to common feature nodes. You can also search for information: press F1 to open the **Help** window or Ctrl+F1 to open the **Documentation** window.

Where Do I Access the Documentation and Application Libraries?

A number of internet resources have more information about COMSOL, including licensing and technical information. The electronic documentation, topic-based (or context-based) help, and the application libraries are all accessed through the COMSOL Desktop.

If you are reading the documentation as a PDF file on your computer, the blue links do not work to open an application or content referenced in a different guide. However, if you are using the Help system in COMSOL Multiphysics, these links work to open other modules, application examples, and documentation sets.

THE DOCUMENTATION AND ONLINE HELP

The *COMSOL Multiphysics Reference Manual* describes the core physics interfaces and functionality included with the COMSOL Multiphysics license. This book also has instructions about how to use COMSOL Multiphysics and how to access the electronic Documentation and Help content.

Opening Topic-Based Help

The Help window is useful as it is connected to the features in the COMSOL Desktop. To learn more about a node in the Model Builder, or a window on the Desktop, click to highlight a node or window, then press F1 to open the Help window, which then displays information about that feature (or click a node in the Model Builder followed by the **Help** button (?). This is called *topic-based* (or *context) help*.

Win

To open the **Help** window:

- In the **Model Builder**, **Application Builder**, or **Physics Builder** click a node or window and then press F1.
- On any toolbar (for example, **Home**, **Definitions**, or **Geometry**), hover the mouse over a button (for example, **Add Physics** or **Build All**) and then press F1.
- From the **File** menu, click **Help** (?).
- In the upper-right corner of the COMSOL Desktop, click the **Help** (?) button.

Mac

Linux

To open the **Help** window:

- In the **Model Builder** or **Physics Builder** click a node or window and then press F1.
- On the main toolbar, click the **Help** (?) button.
- From the main menu, select **Help>Help**.

Opening the Documentation Window

Win

To open the **Documentation** window:

- Press Ctrl+F1.
- From the **File** menu select **Help>Documentation** ( ).

Mac

Linux

To open the **Documentation** window:

- Press Ctrl+F1.
- On the main toolbar, click the **Documentation** ( ) button.
- From the main menu, select **Help>Documentation**.

THE APPLICATION LIBRARIES WINDOW

Each model or application includes documentation with the theoretical background and step-by-step instructions to create a model or application. The models and applications are available in COMSOL Multiphysics as MPH files that you can open for further investigation. You can use the step-by-step instructions and the actual models as templates for your own modeling. In most models, SI units are used to describe the relevant properties, parameters, and dimensions, but other unit systems are available.

Once the Application Libraries window is opened, you can search by name or browse under a module folder name. Click to view a summary of the model or application and its properties, including options to open it or its associated PDF document.

The Application Libraries Window in the *COMSOL Multiphysics Reference Manual.*

Opening the Application Libraries Window

To open the **Application Libraries** window ( ):

Win

- From the **Home** toolbar, **Windows** menu, click ( ) **Applications Libraries**.
- From the **File** menu select **Application Libraries**.

To include the latest versions of model examples, from the **File>Help** menu, select ( ) **Update COMSOL Application Library**.

Mac

Linux

Select **Application Libraries** from the main **File>** or **Windows>** menus.

To include the latest versions of model examples, from the **Help** menu select ( ) **Update COMSOL Application Library**.

CONTACTING COMSOL BY EMAIL

For general product information, contact COMSOL at info@comsol.com.

COMSOL ACCESS AND TECHNICAL SUPPORT

To receive technical support from COMSOL for the COMSOL products, please contact your local COMSOL representative or send your questions to support@comsol.com. An automatic notification and a case number are sent to you by email. You can also access technical support, software updates, license information, and other resources by registering for a COMSOL Access account.

COMSOL ONLINE RESOURCES

COMSOL website	www.comsol.com
Contact COMSOL	www.comsol.com/contact
COMSOL Access	www.comsol.com/access
Support Center	www.comsol.com/support
Product Download	www.comsol.com/product-download
Product Updates	www.comsol.com/support/updates
COMSOL Blog	www.comsol.com/blogs
Discussion Forum	www.comsol.com/community
Events	www.comsol.com/events
COMSOL Application Gallery	www.comsol.com/models
COMSOL Video Gallery	www.comsol.com/video
Support Knowledge Base	www.comsol.com/support/knowledgebase

Overview of the User's Guide

The *Chemical Reaction Engineering Module User's Guide* is a consummate guide to using COMSOL Multiphysics and the add-on module Chemical Reaction Engineering Module. The information in this guide is specific for this module. Instructions how to use COMSOL in general are included with the *COMSOL Multiphysics Reference Manual*. The *Introduction to the Chemical Reaction Engineering Module* contains a quick-start guide to help you get started using this module.

As detailed in the section Where Do I Access the Documentation and Application Libraries? this information can also be searched from the COMSOL Multiphysics software **Help** menu.

THE CHEMISTRY AND REACTION ENGINEERING INTERFACES

The Reaction Engineering Interface, which is found under the Chemical Species Transport branch, has all of the tools required to simulate chemical reaction kinetics, is described in detail for the Theory for the Reaction Engineering and Chemistry Interfaces.

THE CHEMICAL SPECIES TRANSPORT INTERFACES

The transport and conversion of chemical compounds is denoted as chemical species transport. Chemical Species Transport Interfaces chapter describes the Transport of Diluted Species, Transport of Diluted Species in Porous Media, and Transport of Concentrated Species interfaces, which are used for the simulation of chemical reactions, and mass chemical compounds transport through diffusion, convection and electromigration. It also includes the Surface Reactions interface, which models reactions involving surface adsorbed species and species in the bulk of a reacting surface. The Nernst-Planck, The Electrophoretic Transport, Reacting Flow, Laminar Flow, and Transport of Diluted Species in Porous Media interfaces are also described in this chapter.

The Reacting Flow in Porous Media Multiphysics Interface section, the Reacting Flow in Porous Media (rfds) and Reacting Flow in Porous Media (rfcs) interfaces are described. The theory for these physics interfaces is included.

Overview of Chemical Species Transport Interfaces helps you select the best physics interface to use. The rest of the chapter describes the physics interfaces in detail as well as the underlying theory.

THE FLUID FLOW INTERFACES

Fluid Flow Interfaces chapter describes the physics interfaces under the Porous Media and Subsurface Flow branch, which are the Darcy's Law, Brinkman Equations, and Free and Porous Media Flow interfaces. To help you select the physics interface to use, see Modeling Fluid Flow.

THE HEAT TRANSFER INTERFACES

The chapter describes The Heat Transfer in Porous Media Interface and includes a section to help choose the right physics interface (Modeling Heat Transfer).

THERMODYNAMICS INPUT

The chapter Thermodynamics describes how to use the thermodynamics functionality to define thermo-physical and transport properties. The properties in turn can be used when simulating chemical reaction systems, or any type of transport model involving mass transfer, fluid flow, or heat transfer.

2

The Chemistry and Reaction Engineering Interfaces

This chapter describes the **Chemistry (chem)** and **Reaction Engineering (re)** interfaces, available in the **Chemical Species Transport** branch ( ).

In this chapter:

- Overview of the Reaction Engineering and Chemistry Interfaces
- Theory for the Reaction Engineering and Chemistry Interfaces
- The Reaction Engineering Interface
- The Chemistry Interface
- Study Steps for the Reaction Engineering Interface

See also Chemical Species Transport Interfaces for the additional physics interfaces in the **Chemical Species Transport** branch ( ).

Overview of the Reaction Engineering and Chemistry Interfaces

The **Reaction Engineering** and **Chemistry** interfaces share many common features and functionality for defining species and reactions. The main difference is that the **Reaction Engineering** interface always is defined within the context of a (zero dimensional) *reactor model*, solving for a number of species dependent variables and an optional heat balance, whereas the **Chemistry** interfaces solely defines a number of *variable expressions*, based on species and reactions, that can be used when coupling the **Chemistry** interface to, for instance, a space-dependent mass transport model.

THE REACTION ENGINEERING INTERFACE

The Reaction Engineering Interface ( ) includes all of the tools required to simulate chemical reaction kinetics in well-defined environments. This includes the automatic set up and simulation of reversible, equilibrium, and irreversible reactions in volumes or on surfaces. A library of predefined reactors is also available, including batch, continuous stirred-tank, semibatch, and plug flow reactors (see Reactor Types in the Reaction Engineering Interface). In addition, the Parameter Estimation feature makes it possible to evaluate kinetic and model parameters from experimental data.

Use the Generate Space-Dependent Model node to create a space-dependent model based on your model created in the Reaction Engineering interface. This automatically sets up the mass balances and source terms for systems where reactions occur, with a copy of all and your original species and reaction definitions recreated in separate a Chemistry node.

The Reaction Engineering interface can also be used for defining and simulating thermodynamic data.

Interfaces to internal or external thermodynamic packages (such as CAPE-OPEN compliant packages), and an import feature for CHEMKIN® files, mean that the thermodynamic properties within reaction kinetics, as well as mass and heat transfer applications, can be described by empirical relations and algebraic expressions. Also see the Theory for the Reaction Engineering and Chemistry Interfaces.

THE CHEMISTRY INTERFACE

The Chemistry Interface ( ) is a tool for generating a set of variables to be used for modeling chemical species and reactions systems. The variables are generated from species and reaction properties and can be divided in two categories:

- Rate expressions and heat sources for use in mass and heat balances
- Material property variables (mixture density, diffusivities, viscosity, etc.) for use in space-dependent transport equations.

The **Chemistry** interface is also created when the Generate Space-Dependent Model feature is used in The Reaction Engineering Interface, collecting all mixture variables and properties for use in a space-dependent model.

Using the Reaction Node

In each Reaction node, specify the reaction **Formula** and **Reaction type** of a single chemical reaction.

For each reaction formula entered, specify the reaction type with a delimiter separating the two sides of the equation:

- <=> denotes a reversible reaction
- => denotes an irreversible reaction
- = denotes a reaction at chemical equilibrium

It is also possible to adjust the reaction type with the **Reaction type** list (Figure 2-1).

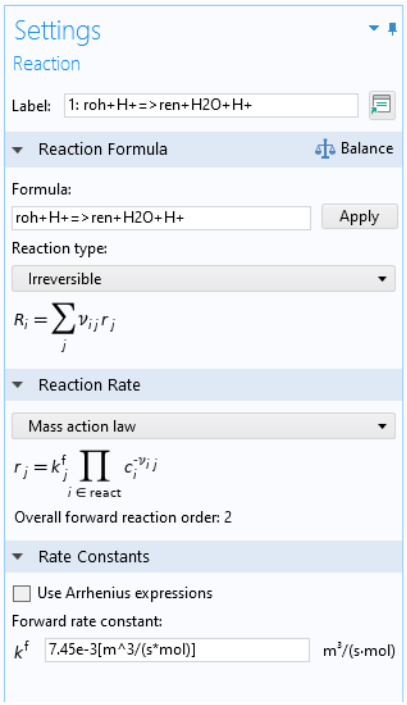


Figure 2-1: After adding a Reaction node, enter the chemical reaction formula and specify the reaction type.

Right-click any Reaction node to disable and enable the corresponding node in the **Model Builder**. Creating reaction subsets in this way is a straightforward approach to investigate the influence of individual reactions on the overall reaction system. Species that take part only in deactivated reactions are automatically deactivated, as indicated by the unavailable Species feature nodes. If a reaction is deleted, the interface automatically deletes those species that take part only in the deleted reactions.

ABOUT REACTION IDENTIFICATION NUMBERS, VARIABLE SCOPE, AND LABELING

When chemical formulas are entered, each reaction is associated with a unique ID (identification) number (Figure 2-2). The ID number is not a row number but rather an absolute reference number to a given reaction. This means that a reaction keeps its ID number, even if reactions are deleted with a lower number. Furthermore, constants

and expressions within fields associated with a given reaction are also indexed with the reaction number.

The **Name** prepended to the variable name is called the variable scope. Defaults are `re` and `chem` for the Reaction Engineering and Chemistry interface, respectively. All variables set up by the interface are given the same scope. The variable scope can be useful to couple the equations of different physics interfaces.

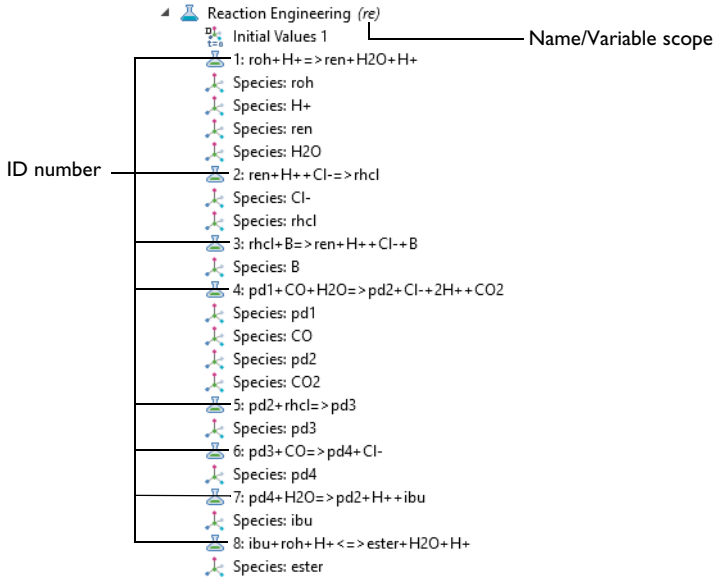


Figure 2-2: The ID number of each Reaction node is displayed in front of the reaction formula.

As a general labeling rule, the variable name that refers to the contents of a field associated with a Reaction node is given by the physics interface **Name**, followed by the field name, and ends with the reaction ID number. For example, the contents of the reaction rate field **r** for Reaction 1 is assigned the variable name `re.r_1`.

	For an example of how to use variables with scope, see *Tank Series with Feedback Control*: Application Library path **Chemical_Reaction_Engineering_Module/Ideal_Tank_Reactors/tankinseries_control**

Using the Species Node

The Reaction Engineering Interface and The Chemistry Interface generate **Species** nodes in the **Model Builder** based on the chemical reaction formulas entered in the **Settings** window for **Reaction**.

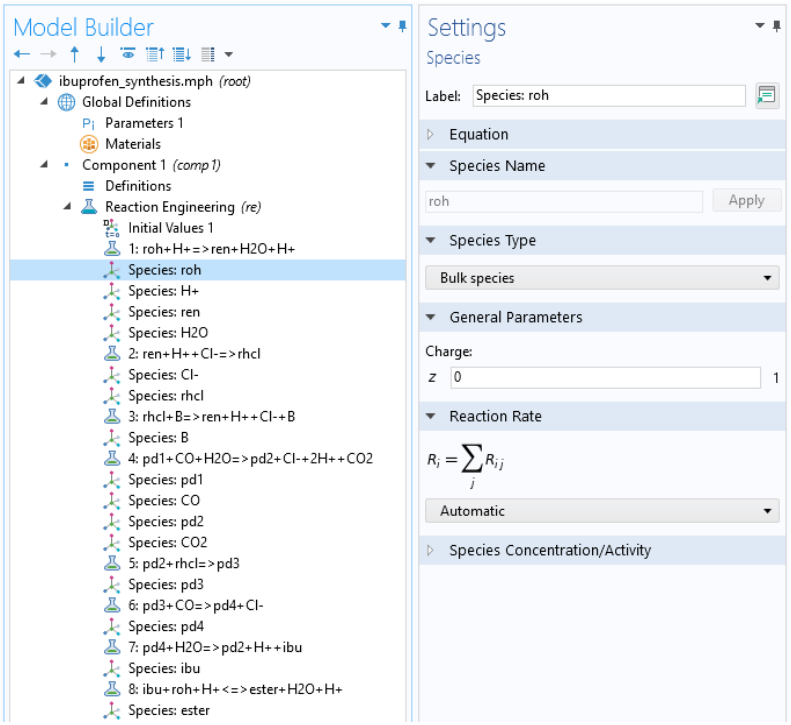


Figure 2-3: Species nodes are generated automatically as chemical reaction formulas are entered in the Reaction nodes.

As with Reaction features you can add, remove, or deactivate Species features by right-clicking a node in the Model Builder. Deactivation of a species automatically deactivates any reactions in which the species is participating.

In the Reaction Rate section it is possible to alter the definition of the reaction rate of the species. This will override the settings in the Reaction feature, where the rate is defined by the stoichiometry of the reaction(s) in which the species participates.

It is also possible to add individual **Species** nodes with either reactive or non-reactive species.

CHOOSING THE SPECIES TYPE

For each species entered, it is possible to change its characteristics by selecting its species type — **Bulk species**, **Surface species**, or **Solvent**.

The **Species type** selection has implications in the calculation of thermodynamic and transport properties.

Bulk species and **Surface species**, defined per reactor volume and area, respectively, set the mixture's physical properties dependent upon its composition. However, configuring a species as a **Solvent** sets the physical properties of the reacting fluid mixture equal to those of the solvent species; specifically, its density, heat capacity, viscosity, and thermal conductivity. The interface also implements a solute-solvent approximation for the interaction of species in the fluid and describes the 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 the 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.

The **Species type** has implications on the Generate Space-Dependent Model procedure since it determines whether interfaces using a solvent-solute approximation of the reacting fluid mixture (as in The Transport of Diluted Species Interface) or a full multicomponent description of the reacting fluid mixture (as in The Transport of Concentrated Species Interface) should be generated.

Furthermore, the **Species type** affects the reaction kinetics. **Solvent** sets the species' concentration to a constant value (the initial species concentration). The Reacting Engineering interface does not formulate a mass balance for the solvent species. This setting corresponds to situations where the solvent does not take part in chemical reactions at all, or where it reacts but is present in large excess.

CREATING VALID SPECIES NAMES AND LABELING

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 must 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 double 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** field in the associated Species feature.

Furthermore, it applies that adding **(ads)** directly after the species name creates a surface species named `speciesname_surf`. Additionally, adding **(s)**, **(l)**, or **(g)** creates either a solid, liquid, or gaseous species denoted `speciesname_solid`, `speciesname_liquid`, and `speciesname_gas`, respectively. Note that the fluid Equilibrium Species Vector, gas or liquid, remains the same despite the presence of any of these species in the system.

Similar to the labeling rule applying to Reaction nodes, the variable name referring to the contents of a field associated with a Species node is given by the interface **Name**, followed by the field name, and ending with the species name. For example, the contents of the **Rate expression** field **R** for the species `roh` is assigned the variable name `re.R_roh` (for the Reaction Engineering interface). Access the definition of all the variables used by a specific node by displaying the **Equation View** node. To display the node, click the **Show More Options** button ( ) and select **Equation View** in the **Show More Options** dialog box.

- Theory for the Reaction Engineering and Chemistry Interfaces
- Variable Naming Convention and Namespace

Using the Equation View Node — Reactions and Species

To display the **Equation View** node, click the **Show More Options** button ( ) and select **Equation View** in the **Show More Options** dialog box. Expand any node, for example the Reaction or Species nodes, and click the **Equation View** node to see the page where the definition of all the variables used by a specific node are listed (Figure 2-4).

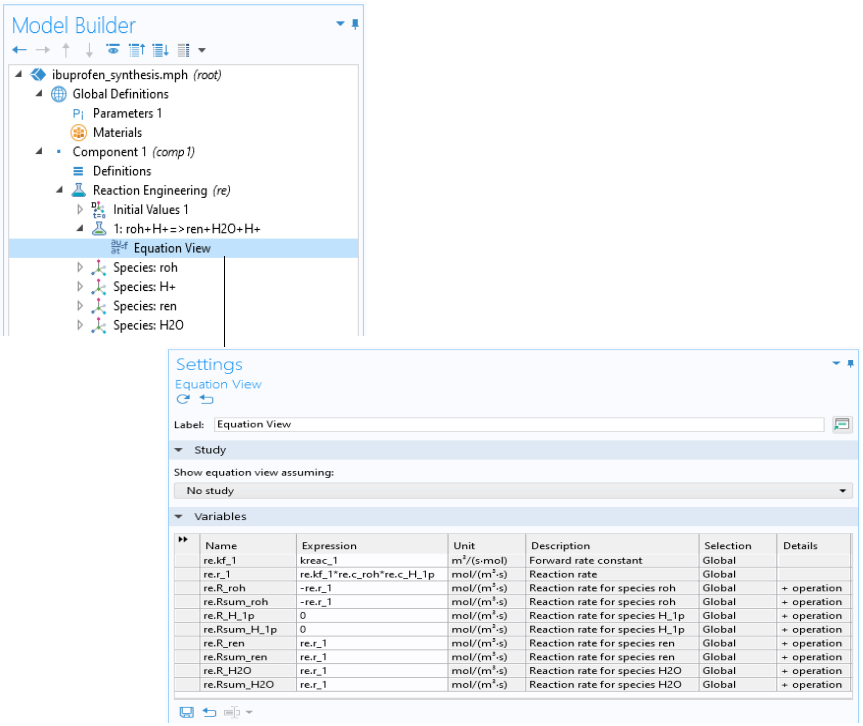


Figure 2-4: The definition of variables used by a node are accessible through the Equation View.

Theory for the Reaction Engineering and Chemistry Interfaces

The Reaction Engineering Interface and The Chemistry Interface theory is described in this section.

- Reactor Types in the Reaction Engineering Interface
- Transport Properties
- CHEMKIN Data and NASA Polynomials
- Working with Predefined Expressions
- References for the Reaction Engineering Interface

Reaction Kinetics and Rate Expressions

The modeling of reactions in COMSOL uses the mass action law by default. Consider a general reaction belonging to a set of j reactions and involving i species:

$$\mathrm{aA} + \mathrm{bB} + \cdots \underset{k_j^r}{\overset{k_j^f}{\rightleftharpoons}} \mathrm{xX} + \mathrm{yY} + \cdots \tag{2-1}$$

For such a reaction set, the reaction rates r_j (SI unit: mol/(m^3·s)) can be described by the mass action law:

$$r_j = k_j^f \prod_{i \in \text{react}} c_i^{-\nu_{ij}} - k_j^r \prod_{i \in \text{prod}} c_i^{\nu_{ij}} \tag{2-2}$$

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 (SI unit: mol/m^3). 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, the temperature dependence of reaction rates can be included by using the predefined Arrhenius expression for the rate constants:

$$k = A\left(\frac{T}{T_{\text{ref}}}\right)^{n} \exp\left(-\frac{E}{R_{\text{g}}T}\right) \tag{2-3}$$

Here, A denotes the frequency factor, n the temperature exponent, E the activation energy (SI unit: 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 $(\text{m}^3/\text{mol})^{\alpha-1}/\text{s}$, where α is the order of the reaction (with respect to volumetric concentrations).

The default settings for the reaction given by Equation 2-1 and assuming equilibrium, yields the equilibrium expression in Equation 2-4:

$$K_{eq} = \frac{c_X^x c_Y^y \cdots}{c_A^a c_B^b \cdots} \tag{2-4}$$

In the case of reversible reactions, it is also possible to make use of equilibrium relationships in order to indirectly calculate reaction constants. For example, calculate the reverse rate constant from the equilibrium condition in this way:

$$k^{\text{r}} = \frac{k^{\text{f}}}{K_{\text{eq}}} \tag{2-5}$$

The Equilibrium Constant

In general, chemical equilibrium is reached when the Gibbs free energy of the system is minimized. The Gibbs free energy of is defined as

$$G(T,P) = U + PV - TS = H - TS \tag{2-6}$$

where U is the internal energy, P is pressure, V is volume, T is temperature, S is entropy and H is enthalpy of the system. For a closed system

$$\mathrm{d}U = \delta Q + \delta W = T\mathrm{d}S - P\mathrm{d}V \tag{2-7}$$

where δQ is (reversible) heat transfer to the fluid and δW is (pressure) work in the system. The change in Gibbs free energy can be written as

$$\mathrm{d}G = T\mathrm{d}S - P\mathrm{d}V + P\mathrm{d}V + V\mathrm{d}P - T\mathrm{d}S - S\mathrm{d}T = V\mathrm{d}P - S\mathrm{d}T \tag{2-8}$$

Chemical potential μ_i is defined as partial molar Gibbs energy for species

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_i \neq n_j} \tag{2-9}$$

where n is the number of mole of species i in the system. At constant temperature, this expression can be integrated as a function of pressure

$$\int_{\mu_i^\circ}^{\mu_i} d\mu = \int_{P^\circ}^{P_i} \hat{v}_i dP \tag{2-10}$$

where v is molar volume and μ_i^o is chemical potential of species at standard state. For an ideal gas this can be expressed as

$$\mu_i - \mu_i^o = R_g T \ln\left(\frac{P_i}{P^o}\right) \tag{2-11}$$

The equilibrium criterion can be written as

$$\sum_i \nu_i \mu_i = 0 \tag{2-12}$$

where ν_i is the stoichiometric coefficient and μ_i is the chemical potential of species i in the reaction. We can evaluate the chemical potential as partial molar Gibbs energy of species in mixture as

$$\mu_i - \mu_i^o = R_g T \ln\left(\frac{\hat{f}_i}{f_i^o}\right) \tag{2-13}$$

where $\hat{f}_i$ is the fugacity of species i in the mixture, and f_i^o is the fugacity of pure species in the standard state. Equation 2-12 can be rewritten as

$$\sum_i \nu_i \mu_i^o + R_g T \ln \prod_i \left(\frac{\hat{f}_i}{f_i^o}\right)^{\nu_i} = 0 \tag{2-14}$$

The equilibrium constant for the reaction, K, is defined as

$$K(T) = \exp\left(\frac{-\Delta G_{rxn}^o}{RT}\right) = \prod_i a_i^{\nu_i} = \prod_i \left(\frac{\hat{f}_i}{f_i^o}\right)^{\nu_i} \tag{2-15}$$

where a_i is the activity of species in the system.

ΔG^o_{rxn} is the Gibbs free energy of reaction (including formation terms) which is defined, in accordance with Equation 2-6, as

$$\Delta G^o_{\text{rxn}} = \Delta H^o_{\text{rxn}} - T\Delta S^o_{\text{rxn}} \tag{2-16}$$

the enthalpy of reaction, ΔH^o_{rxn}, and entropy of reaction, ΔS^o_{rxn}, both at a given temperature T is defined as

$$\Delta H^o_{\text{rxn}}(T) = \sum_i \nu_i \left(\Delta H^o_{f,i} + \int_{T^o}^{T} C_{\text{p},i} dT \right) \tag{2-17}$$

$$\Delta S^o_{\text{rxn}}(T) = \sum_i \nu_i \left(S_{\text{abs},i} + \int_{T^o}^{T} \frac{C_{p,i}}{T} dT \right) \tag{2-18}$$

Here T^o is the temperature at standard state. $\Delta H^o_{f,i}$ and $S_{abs,i}$ are the standard enthalpy of formation and absolute entropy for each species (these data are available in the COMSOL database).

ACTIVITY

Activity of species, a_i is defined by Equation 2-13 as

$$a_i = \exp\left(\frac{\mu_i - \mu_i^o}{R_g T} \right) \tag{2-19}$$

Activity depends on the choice of an arbitrary standard state. The standard state of pure species is usually at 10^5 Pa and for solute in solution is based on hypothetical molality or amount concentration also referred as infinite dilute behavior.

The activity of a species in a mixture is expressed by relationship between dimensionless activity coefficients, γ_i, and measured amount of the species in the system.

$$a_i = \gamma_{x,i} x_i = \gamma_{c,i} \frac{c_i}{c_{\text{ref}}} \tag{2-20}$$

Activity coefficients are usually estimated by Activity coefficient models.

Gas phase

The standard state is the pure species at ideal gas condition, 1 atm and the equilibrium temperature. Activity of species in mixture is expressed by:

$$a_i = \frac{\hat{f}_i}{f_i^o} = \frac{y_i \hat{\phi}_i P}{P^o} \tag{2-21}$$

where $\hat{f}_i$ and $\hat{\phi}_i$ are fugacity and fugacity coefficient of species i in the mixture.

Liquid phase

The standard state is pure liquid species at 1 atm and equilibrium temperature. The fugacity of a species in a mixture is given by

$$\hat{f}_i = y_i \gamma_i f_i \tag{2-22}$$

where γ_i is the activity coefficient of species in the mixture and f_i is the fugacity of pure species at the equilibrium temperature and pressure. The activity is expressed by

$$a_i = \frac{y_i \gamma_i f_i}{f_i^o} \tag{2-23}$$

where f_i^o is the fugacity of pure species at the equilibrium temperature and 1 atm. The ratio f_i/f_i^o is given by

$$\frac{f_i}{f_i^o} = \exp\left(\frac{\hat{v}_i}{R_g T}(P - P_i^{\text{sat}})\right) \tag{2-24}$$

where $\hat{v}_i$ is the partial molar volume of species and P^{sat} is species saturated vapor pressure. For liquids is weak function of pressure and can be assumed to be 1 unless at high pressure.

Dilute Solutions

The concentration can in the case of non-ideal mixtures be replaced with the activity. In these interfaces, the dimensionless activity (a_i) depend on species concentration (c_i), activity coefficient (γ_i) and the standard state concentration (c_{0s}=1 mol/m^3).

$$a_i = \frac{c_i}{c_{0s}} \gamma_i \tag{2-25}$$

Additionally, an effective species concentration ($c_{e,i}$) (SI unit: mol/m^3) is used in the reaction rates (Equation 2-2) when activities are utilized.

$$c_{e,i} = c_i \gamma_i = a_i c_{0s} \tag{2-26}$$

AUTOMATICALLY DEFINED EQUILIBRIUM CONSTANTS

Below the automatically defined equilibrium constants are defined in terms of the equilibrium expression K_{eq}

$$K_{eq} = \prod_i c_i^{\nu_i} = \frac{\prod_{i \in \text{prod}} c_i^{\nu_i}}{\prod_{i \in \text{react}} c_i^{-\nu_i}} \tag{2-27}$$

Gas Phase

Inserting Equation 2-21 in Equation 2-15 gives:

$$K(T) = K_{eq} \prod_i \left(\frac{\hat{\phi}_i P}{c_{sum} P^o} \right)^{\nu_i} \tag{2-28}$$

where for ideal mixtures, the fugacity coefficients $\hat{\phi}_i$ are equal to 1.

Liquid Phase

For low and moderate pressure, the equilibrium constant can be reformulated by substitution of Equation 2-23 to Equation 2-15 as:

$$K(T) = K_{eq} \prod_i \left(\frac{\gamma_i}{c_{sum}} \right)^{\nu_i} \tag{2-29}$$

Handling of Equilibrium Reactions

EXAMPLE 1

The following short example illustrates how the Reaction Engineering interface and the Chemistry interface handle equilibrium reactions in the formulation of the material balance equations.

Consider the reaction:

$$\text{A} \underset{k^r}{\overset{k^f}{\rightleftharpoons}} \text{B} \tag{2-30}$$

According to Equation 2-2 the reaction rate (SI unit: mol/(m^3·s)) is formulated as:

$$r = k^f c_A - k^r c_B$$

where c_A and c_B (SI unit: mol/m^3) are the concentrations of A and B, and k^f and k^r (SI unit: 1/s) are the forward and reverse rate constants, respectively. The net rate expressions with respect to species A and B are then:

$$R_A = -k^f c_A + k^r c_B = -r$$

$$R_B = k^f c_A - k^r c_B = r$$

Assuming the reaction in Equation 2-30 is at equilibrium, the reaction rate r is 0:

$$r = k^f c_A - k^r c_B = 0$$

The relationship between the forward and reverse reaction rates in Equation 2-30 is given by the following ratio:

$$K^{\text{eq}} = \frac{k^f}{k^r} = \frac{c_B}{c_A} \tag{2-31}$$

The Reaction Engineering interface also sets up mass balances that are solved. The general material balances for species A and B, respectively, are:

$$\frac{\partial c_A}{\partial t} = R_A = -r \tag{2-32}$$

$$\frac{\partial c_B}{\partial t} = R_B = r \tag{2-33}$$

The rate of consumption of species A equals the production rate of species B, as shown in Equation 2-32 and Equation 2-33.

With the combined information in Equation 2-32, Equation 2-33, and Equation 2-31, the Reaction Engineering interface is able to define the mass balances for the equilibrium system without the reaction rate expressions. The equation system solved for becomes:

$$\frac{\partial}{\partial t}(c_A + c_B) = 0 \tag{2-34}$$

$$K^{\text{eq}} = \frac{c_B}{c_A} \tag{2-35}$$

In general, for a system of reactions contributing to k mass balances and with j reactions being at equilibrium, the reduced system of equations to be solved is composed of $k - j$ mass balances and j equilibrium expressions. The elimination process producing the above system of equations is automated, allowing simple modeling of chemical equilibrium reactions together with irreversible and/or reversible reactions.

EXAMPLE II

This example shows how equilibrium reactions are considered in the Reaction Engineering interface using the Calculate Transport Properties section.

If two non-equilibrium reactions are taking place in a perfectly mixed isothermal reactor of constant volume:

$$\mathrm{A} \xrightarrow{k_1^f} \mathrm{B}$$

$$\mathrm{B} \underset{k_2^r}{\overset{k_2^f}{\rightleftharpoons}} 2\mathrm{C} \tag{2-36}$$

the corresponding mass balances are:

$$\frac{d}{dt}c_A = -r_1 \tag{2-37}$$

$$\frac{d}{dt}c_B = r_1 - r_2 \tag{2-38}$$

$$\frac{d}{dt}c_C = 2r_2 \tag{2-39}$$

Now compare Equation 2-37, Equation 2-38, and Equation 2-39 with the balance equations that the physics interface sets up for the related chemistry, where the second reaction is instead an equilibrium reaction:

$$\mathrm{A} \xrightarrow{k_1^f} \mathrm{B} \tag{2-40}$$

$$\mathrm{B} \underset{}{\overset{K_2^{eq}}{\rightleftharpoons}} 2\mathrm{C} \tag{2-41}$$

In contrast to the reversible reaction given by Equation 2-36, to make use of the information contained in the equilibrium relation, the mass balances must be reformulated. Mass balances set up for the reactions given by Equation 2-40 and Equation 2-41 are then:

$$\frac{\mathrm{d}}{\mathrm{d}t}c_{\mathrm{A}} = -r_1$$

$$\frac{\mathrm{d}}{\mathrm{d}t}(2c_{\mathrm{B}} + c_{\mathrm{C}}) = 2r_1 \tag{2-42}$$

$$K_2^{\mathrm{eq}} = \frac{c_{\mathrm{C}}^2}{c_{\mathrm{B}}} \tag{2-43}$$

The equilibrium expression (Equation 2-43) introduces an algebraic relationship between the species' concentrations.

Two species, B or C, can be set as Predefined Dependent Species in the Calculate Transport Properties section. Selecting B as the dependent species solves Equation 2-42 for the concentration of C, while B is computed from Equation 2-43.

Reactor Types in the Reaction Engineering Interface

MASS BALANCE

The mass balances that are set up in the Reaction Engineering interface are simplified versions of the general mass transport equation. The main assumption is that the reactor is perfectly mixed, meaning that any variations in compositions within the reactor are neglected.

- Mass Balance Equation

ENERGY BALANCE

The energy balances solved in the Reaction Engineering interface are derived from the general energy balance of a system. The utilized equation follows the perfect mixing assumption and is dependent on the selected reactor as described below.

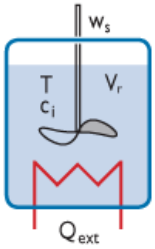
Theory for Heat Transfer

The following reactor types are available in the Reaction Engineering interface (the Chemistry interfaces does not contain reactor models):

- Batch
- Batch, Constant Volume
- CSTR, Constant Mass/Generic
- CSTR, Constant Volume
- Semibatch
- Plug Flow

BATCH

In the batch reactor no mass enters or leaves the system. 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 species mass balances are given by:

$$\frac{d(c_i V_r)}{dt} = V_r R_i \tag{2-44}$$

which takes into account the effect of changing volume. In Equation 2-44, c_i (SI unit: mol/m^3) is the species molar concentration, V_r (SI unit: m^3) denotes the reactor volume, and R_i (SI unit: mol/(m^3·s)) is the species rate expression.

For an ideal reacting gas, the energy balance is:

$$V_r \sum_i c_i C_{p,i} \frac{dT}{dt} = Q + Q_{ext} + V_r \frac{dp}{dt} \quad (2\text{-}45)$$

In Equation 2-45, $C_{p,i}$ (SI unit: J/(mol·K)) is the species molar heat capacity, T (SI unit: K) is the temperature, and p (SI unit: Pa) the pressure. On the right-hand side, Q (SI unit: J/s) is the heat due to chemical reaction, and Q_{ext} (SI unit: J/s) denotes heat added to the system. The heat of reaction is:

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

where H_j (SI unit: J/mol) is the enthalpy of reaction, and r_j (SI unit: mol/(m^3·s)) the reaction rate.

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

$$V_r \sum_i c_i C_{p,i} \frac{dT}{dt} = Q + Q_{ext} \quad (2\text{-}46)$$

Ibuprofen Synthesis: Application Library path **Chemical_Reaction_Engineering_Module/Ideal_Tank_Reactors/ibuprofen_synthesis**

BATCH, CONSTANT VOLUME

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

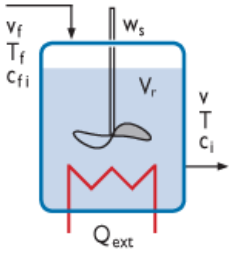
$$\frac{dc_i}{dt} = R_i$$

For an ideal reacting gas, the energy balance is given by Equation 2-45. For an incompressible and ideally mixed reacting liquid, the energy balance is given by Equation 2-46.

Neutralization of Chlorine in a Scrubber: Application Library path **Chemical_Reaction_Engineering_Module/Ideal_Tank_Reactors/chlorine_scrubber**

CSTR, CONSTANT MASS/GENERIC

The continuous stirred tank reactor (CSTR) has reacting species entering and leaving the reactor by means of inlet and outlet streams. The reactor is 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 for the CSTR are given by:

$$\frac{\mathrm{d}(c_i V_\mathrm{r})}{\mathrm{d}t} = \sum_m v_{\mathrm{f},m}\, c_{\mathrm{f},m} - v c_i + R_i V_\mathrm{r} \tag{2-47}$$

In Equation 2-47, $c_{\mathrm{f},m}$ (SI unit: mol/m^3) is the species molar concentration of the associated feed inlet stream $v_{\mathrm{f},m}$ (SI unit: m^3/s). V_r (SI unit: m^3) denotes the reactor volume and is a function of time.

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

$$\frac{\mathrm{d}V_\mathrm{r}}{\mathrm{d}t} = \sum_m v_{\mathrm{f},m} - v + v_\mathrm{p} \tag{2-48}$$

In Equation 2-48, v_p (SI unit: m^3/s) denotes the volumetric production rate. It is given by Equation 2-49 for ideally mixed liquids and by Equation 2-50 for ideal gases.

$$v_\mathrm{p} = V_\mathrm{r} \sum_i \frac{R_i M_i}{\rho_i}, \quad R_i = \sum_j \nu_{ij} r_j \tag{2-49}$$

$$v_\mathrm{p} = \frac{R_\mathrm{g} T}{p} V_\mathrm{r} \sum_i R_i \tag{2-50}$$

where ν_{ij} is the stoichiometric coefficient of species i in reaction j, M_i (SI unit: kg/mol) denotes the species molecular weight, ρ_i (SI unit: kg/m^3) the species density, and R_i (SI unit: mol/(m^3·s)) is the reaction rate of species i.

When this reactor model is solved for constant mass, the reactor model assumes that the volumetric flow rate of the outlet stream, v (SI unit: m^3/s), is adjusted in such a way that the total mass of the reactor is held constant:

$$v = \frac{\sum_m v_{\mathrm{f},m}\rho_{\mathrm{f},m}}{\rho} \tag{2-51}$$

In contrast, when the model is set to be solved for generic conditions a specific outlet flow stream can be set.

The energy balance for an ideal reacting gas is:

$$V_\mathrm{r}\sum_i c_i C_{\mathrm{p},i}\frac{\mathrm{d}T}{\mathrm{d}t} = Q + Q_\mathrm{ext} + V_\mathrm{r}\frac{\mathrm{d}p}{\mathrm{d}t} + \sum_m\sum_i v_{\mathrm{f},mi}\, c_{\mathrm{f},mi}(h_{\mathrm{f},mi} - h_i) \tag{2-52}$$

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

$$V_\mathrm{r}\sum_i c_i C_{\mathrm{p},i}\frac{\mathrm{d}T}{\mathrm{d}t} = Q + Q_\mathrm{ext} + \sum_m\sum_i v_{\mathrm{f},mi}\, c_{\mathrm{f},mi}(h_{\mathrm{f},mi} - h_i) \tag{2-53}$$

Ideal Stirred Tank Reactor System: Application Library path **Chemical_Reaction_Engineering_Module/Ideal_Tank_Reactors/tank_flow_system**

CSTR, CONSTANT VOLUME

This reactor type is a CSTR reactor where the reactor volume is constant.

The species mass balances are given by:

$$\frac{\mathrm{d}(c_i V_r)}{\mathrm{d}t} = \sum_m v_{\mathrm{f},m}\, c_{\mathrm{f},m} - v c_i + R_i V_\mathrm{r} \tag{2-54}$$

Assuming constant reactor volume:

$$\frac{\mathrm{d}V_\mathrm{r}}{\mathrm{d}t} = 0$$

and setting the volumetric outlet rate to:

$$v = \sum_m v_{\mathrm{f},m} + v_{\mathrm{p}} \tag{2-55}$$

Equation 2-54 can be rewritten as:

$$V_{\mathrm{r}} \frac{\mathrm{d}c_i}{\mathrm{d}t} = v_{\mathrm{f},i}\, c_{\mathrm{f},i} - \left(\sum v_{\mathrm{f},i} + v_{\mathrm{p}}\right) c_i + R_i V_{\mathrm{r}} \tag{2-56}$$

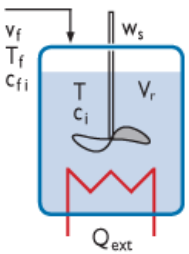
The volumetric production rate, v_{p}, is defined as in Equation 2-49 and Equation 2-50.

The energy balance is the same as for the CSTR with Constant Mass/Generic reactor type (Equation 2-53).

Startup of a Continuous Stirred Tank Reactor: Application Library path **Chemical_Reaction_Engineering_Module/Tutorials/cstr_startup**

SEMIBATCH

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



The species mass balances are given by:

$$\frac{\mathrm{d}(c_i V_{\mathrm{r}})}{\mathrm{d}t} = v_{\mathrm{f},i}\, c_{\mathrm{f},i} + R_i V_{\mathrm{r}} \tag{2-57}$$

The reactor volume is a function of time given by:

$$\frac{\mathrm{d}V_{\mathrm{r}}}{\mathrm{d}t} = \sum_m v_{\mathrm{f},m} + v_{\mathrm{p}} \tag{2-58}$$

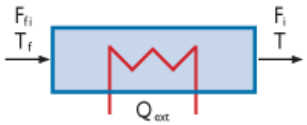
The volumetric production rate, v_p, is defined as in Equation 2-49 and Equation 2-50.

An energy balance over the Semibatch reactor results in the same energy balance expression as for the CSTR reactor types (Equation 2-53).

	Semibatch Polymerization: Application Library path **Chemical_Reaction_Engineering_Module/Ideal_Tank_Reactors/semibatch_polymerization**

PLUG FLOW

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



The species mass balances are given by:

$$\frac{dF_i}{dV} = R_i \tag{2-59}$$

where F_i (SI unit: mol/s) is the species molar flow, V (SI unit: m^3) is the reactor volume, and R_i (SI unit: mol/(m^3·s)) denotes the species rate expression.

In order to evaluate the rate expressions R_i, which are functions of the species concentrations, the physics interface calculates:

$$c_i = \frac{F_i}{v}$$

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

For liquids, the volumetric flow rate is given by:

$$v = \sum_i \frac{F_i M_i}{\rho_i}$$

where M_i (SI unit: kg/mol) denotes the species molecular weight and ρ_i (SI unit: kg/m^3) the species density

For ideal gases:

$$v = \frac{R_g T}{p} \sum_i F_i$$

so that

$$c_i = \frac{p}{R_g T} \frac{F_i}{\sum_i F_i}$$

where p (SI unit: Pa) is the constant pressure.

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

$$\sum_i F_i C_{p,i} \frac{dT}{dV} = Q + Q_{ext} \quad (2\text{-}60)$$

Equation 2-60 is similar to the energy balance for the batch reactors (Equation 2-46), but with a reactor volume dependence instead of a time dependence.

Nonisothermal Plug-Flow Reactor: Application Library path
Chemical_Reaction_Engineering_Module/Tutorials/nonisothermal_plug_flow

Transport Properties

The Reaction Engineering Interface and The Chemistry Interface can calculate several transport properties that can be accessed in interfaces in space dependent models.

DIFFUSIVITY

The diffusivity is calculated in terms of binary diffusion coefficients. These are available for the following fluid mixtures:

Gases with or without Solvent

The diffusion coefficients are calculated from the following expression based on kinetic gas theory (Ref. 7):

$$D_{AB} = 2.628 \cdot 10^{-22} \cdot \frac{\sqrt{T^3(M_A + M_B)/(2 \cdot 10^3 M_A M_B)}}{p\sigma_A\sigma_B} \cdot \Omega_D^{-1} \tag{2-61}$$

Here, D_{AB} (SI unit: m^2/s) is the binary diffusion coefficient, M (SI unit: kg/mol) equals the molecular weight, T (SI unit: K) represents the temperature, p (SI unit: Pa) is the pressure, and σ (SI unit: m) equals the characteristic length of the Lennard-Jones/ Stockmayer potential. In addition, Ω_D is the collision integral, given by the relation of Neufeld et al. (Ref. 6):

$$\Omega_D = \frac{c_1}{(T^*)^{c_2}} + \frac{c_3}{\exp(c_4 T^*)} + \frac{c_5}{\exp(c_6 T^*)} + \frac{c_7}{\exp(c_8 T^*)} \tag{2-62}$$

where the reduced temperature is:

$$T^* = T\frac{k_b}{\sqrt{\varepsilon_A \varepsilon_B}} \tag{2-63}$$

In Equation 2-62, c_x are empirical constants, μ_D is the species dipole moment value (SI unit: Cm) and ε/k_b (SI unit: K) the potential energy minimum value divided by Boltzmann's constant. Tabulated data in literature frequently lists values of ε/k_b rather than ε. It should be noted that predefined expressions for binary diffusivities only treat ideal gas mixtures. Thus, these are applicable as input only for gases at moderate pressure in multicomponent diffusive transport models.

The binary diffusivity according to Equation 2-61 is also suited for gaseous species in solvent, simply by setting either the component A or B to the solvent. The binary diffusion coefficient is in this case equal to the diffusion coefficient of the bulk species.

Liquid with Solvent

The diffusivity of a species A in a solvent B is calculated with the Wilke-Chang equation (Ref. 8):

$$D_{AB} = 3.7 \cdot 10^{-15} \frac{(\phi_B M_B)^{1/2} T}{\mu_B V_{b,A}^{0.6}} \tag{2-64}$$

where μ_B (SI unit: N·s/m^2) denotes the solvent's dynamic viscosity (see Equation 2-69), and $V_{b,A}$ (SI unit: m^3/mol) equals the molar volume at the normal boiling point of the solute species. ϕ_B is the dimensionless association factor of the solvent, which by default is set to 1.

DYNAMIC VISCOSITY

The dynamic viscosities are computed for the following fluid mixtures:

Gases with Solvent

The dynamic viscosity of the mixture is assumed to be the same as that of the solvent. This is given by the kinetic gas theory (Ref. 6 and Ref. 7), with species i being the solvent:

$$\mu = 2.669 \cdot 10^{-6} \frac{\sqrt{T(M_i \cdot 10^3)}}{\sigma_i^2} \Omega_D^{-1} \tag{2-65}$$

In Equation 2-65, μ (SI unit: Ns/m^2) represents the dynamic viscosity, and Ω_D is the dimensionless collision integral given by:

$$\begin{aligned} \Omega_D = {} & b_1 (T/(\varepsilon_i/k_b))^{-b_2} + b_3[\exp(-b_4 T/(\varepsilon_i/k_b))] \\ & + b_5[\exp(-b_6 T/(\varepsilon_i/k_b))] + \frac{(4.998 \cdot 10^{-40})\mu_{D,i}^4}{k_b^2 T(\varepsilon_i/k_b)\sigma_i^6} \end{aligned} \tag{2-66}$$

In Equation 2-65 and Equation 2-66, b_x are empirical constants, μ_D (SI unit: Cm) the species dipole moment value, and ε/k_b (SI unit: K) the potential energy minimum value divided by Boltzmann's constant. Tabulated data in literature frequently lists values of ε/k_b rather than ε, and σ (SI unit: Å) is the characteristic length value.

Gases without Solvent

The dynamic viscosity of gas mixtures without solvent are calculated according to Ref. 9 with the following expression:

$$\mu = \sum_{i=1}^{n} \left(\frac{\mu_i}{1 + \frac{1}{x_i} \sum_{j=1, j \neq i}^{j=n} x_j \phi_{ij}} \right) \tag{2-67}$$

where ϕ_{ij} is defined as:

$$\phi_{ij} = \frac{[1 + (\mu_i/\mu_j)^{0.5}(M_j/M_i)^{0.25}]^2}{(2\sqrt{2})[1 + M_i/M_j]^{0.5}} \quad (2\text{-}68)$$

In Equation 2-67 and Equation 2-68, x_i is the molar composition and μ_i is computed with Equation 2-65 for each of the species in the mixture.

Liquid with Solvent

The dynamic viscosity of the mixture is assumed to the same as that of the solvent. An approximate expression for the temperature dependence of the dynamic viscosity is given by (Ref. 3):

$$\mu = 10^{-3}\left((\mu_{\text{ref}}10^3)^{-0.2661} + \frac{T - T_{\text{ref}}}{223}\right)^{-3.758} \quad (2\text{-}69)$$

where μ (SI unit: Ns/m^2) is the dynamic viscosity. As inputs for Equation 2-69, the physics interface takes the reference viscosity, μ_{ref} (SI unit: Pa·s) at the reference temperature T_{ref} (SI unit: K).

THERMAL CONDUCTIVITY

The thermal conductivity is calculated as well for some types of fluid mixtures:

Gas With or Without Solvent

The predefined expression for thermal conductivity comes from the Stiel-Thodos equation (Ref. 10), which is defined as:

$$k = \frac{\mu}{M}(1.15C_{\text{p}} + 0.88R_{\text{g}}) \quad (2\text{-}70)$$

where k (SI unit: W/(m·K)) is the thermal conductivity and C_p (SI unit: J/(mol·K)) denotes the molar heat capacity. Equation 2-70 is a function of viscosity, μ, as given by Equation 2-65. Equation 2-70 is directly used in the case of a solvent; all parameters being those of the solvent. Without a solvent, however, the following equation is also used:

$$k = \frac{1}{2}\left[\sum_{i=1} x_i k_i + \left(\sum_{i=1} \frac{x_i}{k_i}\right)^{-1}\right]$$

where k_i is the thermal conductivity of each species i and x_i the molar composition for each of the species in the mixture.

CHEMKIN Data and NASA Polynomials

CHEMKIN® files can be used to import data for simulation of complex chemical reactions in the gas phase. These input files may contain three basic sets of information — chemical kinetics, species thermodynamic properties, and species transport properties for either volumetric or surface species. Use imported data to set up and do the following:

- Solve mass and energy balances for ideal reactor systems (reactors, semi- reactors, CSTRs, and plug flow reactors).
- Evaluate species transport properties as a function of reactor conditions.
- Evaluate mass, energy, and momentum balances for space-dependent models, and transfer them to COMSOL Multiphysics.

It is possible to read the input files for kinetics, thermodynamic, and transport properties independently and use these as separate data resources. For example, if a set of reactions is entered into the Reaction Engineering interface, species thermodynamic and transport data can be supplied by reading the appropriate input files. The full functionality of the physics interface 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.

The following CHEMKIN files are compatible:

- Transport CHEMKIN files that supply data used to compute Transport Properties.
- Thermodynamic CHEMKIN files containing data for Gordon and McBride or NASA polynomials (Ref. 4). These polynomials are denoted *NASA format* and compute the species' heat capacity, $\mathbf{C_p}$, molar enthalpy, **h**, and molar entropy, **s**:

$$C_{\mathrm{p},i} = R_{\mathrm{g}}(a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4) \tag{2-71}$$

$$h_i = R_{\mathrm{g}}\left(a_1T + \frac{a_2}{2}T^2 + \frac{a_3}{3}T^3 + \frac{a_4}{4}T^4 + \frac{a_5}{5}T^5 + a_6\right) \tag{2-72}$$

$$s_i = R_{\mathrm{g}}\left(a_1\ln T + a_2T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7\right) \tag{2-73}$$

Here:

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

From the CHEMKIN files the coefficients a_1 to a_7 are directly imported into the corresponding NASA format fields. Coefficients for NASA polynomials are available as public resources (Ref. 11).

Kinetics CHEMKIN files that can be imported in the Reversible Reaction Group feature. These consist of reaction kinetics data, such as activation energy (SI unit: J/mol).

	Homogeneous Charge Compression Ignition of Methane: Application Library path **Chemical_Reaction_Engineering_Module/Ideal_Tank_Reactors/compression_ignition**
	NOx Reduction in a Monolithic Reactor: Application Library path **Chemical_Reaction_Engineering_Module/Tutorials/monolith_3d**
	Chemical Vapor Deposition of GaAs: Application Library path **Chemical_Reaction_Engineering_Module/Reactors_with_Mass_and_Heat_Transfer/gaas_cvd**

Working with Predefined Expressions

You can choose whether to use the predefined expressions as given, use parts of a predefined set of expressions, or replace expressions entirely. A few short examples highlight the use of the predefined expressions used in the Species Transport Expressions and Species Thermodynamic Expressions sections to enter the thermodynamic properties of carbon monoxide. The sections also illustrate the possibility to adapt to different modeling situations.

CASE I

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 2-71); use the predefined expression h for each species to calculate the heat of reaction (Equation 2-72); and use the predefined expression s for each species to calculate the entropy of reaction (Equation 2-73) and subsequently the equilibrium constant of reaction (See Handling of Equilibrium Reactions).

To accomplish this, enter the seven coefficients of the NASA format, a_1 to a_7, into the appropriate fields, or import a CHEMKIN Import for Species Properties thermo input 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 2-98).

Polynomials for C_p are available in the literature (Ref. 2, Ref. 3, and Ref. 5) in the frequently used form

$$C_\mathrm{p} = R_\mathrm{g} \sum_n a_n T^{n-1} \qquad n = 1, \ldots, 5$$

You can directly use the predefined expression for the species' heat capacity, Equation 2-71, also given in the **C_p** field, by supplying coefficients in the **a_1** to **a_5** fields.

You also want to use the predefined expressions h for each species to calculate the heat of reaction (Equation 2-72). 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 2-72 is straightforward. In the NASA polynomial format, the species molar enthalpy is related to its heat capacity according to

$$h = \int_0^T C_\mathrm{p} dT + h(0) \tag{2-74}$$

Inserting Equation 2-71 into Equation 2-74, and comparing the result with Equation 2-72, 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_std = 298.15 K, which is given by

$$a_6 = \frac{h(T_\mathrm{std})}{R_\mathrm{g}} - \left(a_1 T_\mathrm{std} + \frac{a_2}{2} T_\mathrm{std}^2 + \frac{a_3}{3} T_\mathrm{std}^3 + \frac{a_4}{4} T_\mathrm{std}^4 + \frac{a_5}{5} T_\mathrm{std}^5 \right) \tag{2-75}$$

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

$$h = C_p(T - 298\ \text{K}) + h(298\ \text{K})$$

References for the Reaction Engineering Interface

1. H.G. Rackett, "Equation of State for Saturated Liquids," *J. Chem. Eng. Data*, vol. 15, no. 4, pp. 514–517, 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. 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.

5. M. Zabransky, V. Ruzicka Jr., V. Majer, and E.S. Dolmaski, "Heat Capacity of Liquids: Critical Review and Recommended Values," *J. Phys. Chem. Ref. Data Volume I and II, Monograph, No. 6*, 1996.

6. P.D. Neufeld, A.R. Janzen, and R.A. Aziz, "Empirical Equations to Calculate 16 of the Transport Collision Integrals $\Omega^{(l,s)*}$ for the Lennard-Jones (12-6) Potential," *J. Chem. Phys.*, vol. 57, pp. 1100–1102, 1972.

7. R.S. Brokaw, "Predicting Transport Properties of Dilute Gases," *Ind. Eng. Process Design Develop.*, vol. 8, no. 2, pp. 240–253, 1969.

8. C.R. Wilke and P. Chang, "Correlation of Diffusion Coefficients in Dilute Solutions," *AIChE J.*, vol. 1, no. 2, pp. 264–270, 1955.

9. C. R. Wilke, "A Viscosity Equation for Gas Mixtures," *J. Chem. Phys.*, vol. 18, no. 4, pp. 517–519, 1950.

10. L.I. Stiel and G. Thodos, "The Viscosity of Polar Substances in the Dense Gaseous and Liquid Regions," *AIChE J.*, vol. 10, p. 26–29, 1964.

11. See, for example, www.comsol.com/chemical-reaction-engineering-module

The Reaction Engineering Interface

The **Reaction Engineering (re)** interface ( ), found under the **Chemical Species Transport** branch ( ) when adding a physics interface, is used to model several chemical reactor types and the evolution of chemical reactions over time. The mass balance and energy balance equations describing these systems assume perfect or well-defined mixing in the reactor. Essentially, the physics interface simulates, tank, and plug flow chemical reactors to investigate the behavior over time of a chemical reaction.

The reaction kinetics expressions of a reactor can be exported to a space-dependent model, using the Generate Space-Dependent Model feature. This gives you the power to simulate reacting systems as they depend on fluid flow, mass transfer, and heat transfer — in other words, including space dependencies.

Add physics features from the toolbar, or right-click **Reaction Engineering** to select features from the context menu. Many of the fields and nodes described in this section are made available when either a Reaction or a Species (or both) subnode is added to the Model Builder. Because nodes and subnodes are accessible at any time, and any change is updated throughout the model, reactions and species are often defined before the settings described in this section.

All predefined constants and expressions can be overwritten by user-defined expressions. This makes it possible to go beyond the modeling assumptions that are the defaults in this physics interface.

- Theory for the Reaction Engineering and Chemistry Interfaces
- Features Nodes Available for the Reaction Engineering Interface

The following is a description of the features and fields available on the **Settings** window for Reaction Engineering.

SETTINGS

The **Label** is the default physics interface name.

The **Name** is used primarily as a scope prefix for variables defined by the physics interface. Refer to such physics interface variables in expressions using the pattern `<name>.<variable_name>`. In order to distinguish between variables belonging to

different physics interfaces, the `name` string must be unique. Only letters, numbers, and underscores (_) are permitted in the **Name** field. The first character must be a letter.

The default **Name** (for the first physics interface in the model setup) is `re`.

EQUATION

This section displays the governing equations according to the selection of reactor types in the **Reactor** section.

REACTOR

Select a **Reactor type** to define the reaction system. The available reactor types are: **Batch**, **Batch, constant volume**, **CSTR, constant volume**, **CSTR, constant mass/generic**, **Semibatch**, and **Plug flow**. Each reactor type solves a mass balance based on properties typical to the type, such as reactor volume, volumetric production, or flow rate:

- Batch: In reactors no mass enters or leaves the system. This type can account for a variable reactor volume.
- Batch, Constant Volume: Same as Batch but where the reactor volume is assumed to be constant. As this is the situation for most reacting systems, this is the default condition.
- CSTR, Constant Mass/Generic: Continuous stirred tank reactors (CSTR) differ from batch reactors, since these allow species to enter and leave the reactor by means of feed inlet streams and outlet streams. The system's volume is allowed to change, such as in a car engine cylinder or a balloon. This reactor model can be solved either for a constant mass condition or by selecting a specific outlet flow.
- CSTR, Constant Volume: Same as the CSTR with constant mass/generic reactor but assumes that the volume is constant during operation.
- Semibatch: Semibatch reactors differ from batch reactors in that they allow reactants to enter the reactor by means of one or several feed inlet streams.
- Plug Flow: In the plug flow reactor, the species concentrations and the temperature vary with position. Plug flow in a tubular configuration means that concentration and temperature gradients develop only in the axial direction, but not in the radial direction.

For each **Reactor type**, additional settings are shown in Table 2-1. If a surface reaction or species is included, except for the **Plug flow** reactor type, the surface reaction area is

also a parameter. The parameters and expressions are used in the mass balance equations.

TABLE 2-1: REACTOR TYPE PARAMETERS

REACTOR TYPE	PARAMETERS TO DEFINE
Batch	Reactor volume V_r
Batch, constant volume	Reactor volume V_r
CSTR, constant mass/generic	Volumetric production rate v_p and Volumetric outlet rate v
CSTR, constant volume	Volumetric production rate v_p and Reactor volume V_r
Semibatch	Volumetric production rate v_p
Plug flow	Volumetric flow rate v

Volumetric Rate

For **CSTR, constant volume** and **Semibatch** reactor types, the **Volumetric production rate** (v_p) is available. For **Automatic**, the in-built **Volumetric production rate** expression is shown. If **User defined** is selected, the expression can be changed (SI unit: m^3/s). For instance, this enables the setting of zero (0) volumetric production rate, which ignores volume changes due to reactions.

- For liquid phase reactions, the **Automatic** expression for the **Volumetric production rate** varies with the reaction rate of each species as defined by:

$$v_p = V_r \sum_i \frac{R_i M_i}{\rho_i}, \quad R_i = \sum_j \nu_{ij} r_j \tag{2-76}$$

  The physics interface automatically inserts the stoichiometric coefficients (ν_{ij}) and reaction rate expressions for each species (R_i) that depend on j number of reactions of a rate (r_j), as defined in the Reaction feature node. Furthermore, the values of the molar mass (M_i) and the species density (ρ_i) are automatically taken from the Species features.

- For gas phase reactions, the **Automatic** expression for the **Volumetric production rate** is similarly given by:

$$v_p = \frac{R_g T}{p} V_r \sum_i R_i, \quad R_i = \sum_j \nu_{ij} r_j \tag{2-77}$$

  For **CSTR, constant mass/generic**, select **Volumetric rate** to either **Constant mass (Automatic)** or **Generic**. The **Constant mass (Automatic)** selection shows both the expression for **Volumetric production rate** (v_p) (Equation 2-77 for gas, or

Equation 2-76 for liquid phase reactions) and **Volumetric outlet rate** (v) (Equation 2-78). The latter is derived from constant mass flow condition through the reactor:

$$v = \frac{\sum_m v_{f,m} \cdot \rho_{f,m}}{\rho} \tag{2-78}$$

The mixture density (ρ_f) of m number of feed inlet streams is determined in the same way as in the **Mixture Properties** section. For **Generic** both the **Volumetric rate** properties can be edited (SI unit: m^3/s). This means that it is possible to completely control the volumetric outlet rate from the CSTR.

For the **Plug flow** reactor, the **Volumetric flow rate** along the reactor is set. The **Automatic** definition computes a variable volumetric flow rate that depends on the molar flow rate of each species (F_i).

- For liquid phase reactions, the expression is:

$$v = \sum_i \frac{F_i M_i}{\rho_i} \tag{2-79}$$

- and for gas phase reactions:

$$v = \frac{R_g T}{p} \sum_i F_i \,. \tag{2-80}$$

The default value for p (**Reactor pressure**) is 1 atm in Equation 2-81 and it is set in the **Mixture Properties** section.

Reactor Volume

This input field sets the **Reactor volume** V_r — that is, the fluid volume in which chemical reaction takes place. The **Batch** reactor type can account for a changing volume, thus a time-dependent volume expression can be entered here.

Surface Reaction Area

Once a surface reaction, or a surface species, has been added, for all reactor types except **Plug flow**, the **Surface reaction area** settings become visible. Here, the area of the

surface on which the surface reactions take place can be defined. The surface area can either be defined directly as a parameter, or by defining the **Surface area to volume ratio**.

Reactor Types in the Reaction Engineering Interface

ENERGY BALANCE

From the list select to **Exclude** or **Include** the energy balance, which in essence determines whether the system is solved for either isothermal or nonisothermal conditions, respectively. The latter introduces the temperature as a variable in the interface.

If **Exclude** is chosen, enter a **Temperature** T for the system.

It is possible to incorporate cooling or heating of the reactor. This is done in **External heating or cooling** (Q_{ext}). Enter a negative value to account for cooling or a positive one for heating (SI unit: W). Note that for the Plug Flow reactor type, the **External heating or cooling** (Q) is defined per reactor volume (SI unit: W/m^3).

MIXTURE PROPERTIES

Thermodynamics

All property parameters and property functions required by the interface can be automatically created by coupling to a system added to the **Thermodynamics** node. To do so click the **Thermodynamics** check box and select an existing Thermodynamic System.

The **Thermodynamics** check box is enabled except if:

- the Thermodynamics node, including one or more systems, is not added under **Global Definitions**, or
- no species are added in the **Reaction Engineering** interface, or
- a CHEMKIN file is imported in the **Reaction Engineering** interface.

Phase

Use the **Phase** list to specify the state of aggregation of the mixture.

Density

This setting is available when the **Calculate mixture properties** check box in the **Calculate Transport Properties** section has been selected.

Two settings are always available for the mixture **Density**: **Automatic** or **User defined**. The **Thermodynamics** options is available when the interface is coupled to a Thermodynamic System, and all interface species has been matched to species in the system. In this case the density is defined by a function automatically added under the thermodynamic system coupled to.

The mixture density is transferred to physics interfaces set up by the Generate Space-Dependent Model feature. The density is compiled for both multicomponent and solute-solvent solutions.

The **Automatic** setting uses the following logic:

- **Automatic** selected for **Liquid**, considers the liquid as ideal and incompressible. The liquid mixture density depends on the density of i number of pure species (ρ_i) and the species mass fraction (w_i).

$$\rho = \frac{1}{\sum_i \frac{w_i}{\rho_i}}$$

  The mass fraction is given by the species concentration (c_i) and the molar mass (M_i).

$$w_i = \frac{c_i M_i}{\sum_i c_i M_i}$$

- **Automatic** set for **Gas** calculates the gas mixture density (ρ) from the concentrations (c_i) and molar masses (M_i) of the mixture species, which are automatically taken from Species features.

$$\rho = \sum_i c_i M_i \tag{2-81}$$

- If a Species Type is set to **Solvent** and the **Mixture** is **Liquid**, the mixture density is the same as the solvent density as defined in **Density** in **General parameters** in the Species node. When **Mixture** is **Gas**, the mixture density is calculated from Equation 2-81 only for the species set as **Solvent**.

Reactor Pressure

The **Phase** - **Gas** setting displays the **Reactor pressure**. For all reactor types, except the **Plug flow** reactor, select either a pressure computed from the **Ideal gas law** or from any

other expression using the **User defined** option. The **Batch** and **Semibatch** reactor types also have the option to keep the reactor pressure **Constant** during reaction.

For the Plug Flow reactor, the **Reactor pressure** can be entered in the case of the **Reactor** section having the **Volumetric rate** set to **Automatic**, in which case the **User defined** alternative is available and a constant pressure fits the conditions.

When the Thermodynamics check box is selected in the **Mixture Properties** section and the species are fully coupled (see the section below), the reactor pressure is set to **Thermodynamics** indicating that it is automatically computed.

SPECIES MATCHING

The **Species Matching** section is activated when the Thermodynamics check box is selected in the **Mixture Properties** section. The species in the Reaction Engineering interface can be matched to species in the Thermodynamic System. This ensures that the arguments in the thermodynamic system functions are correctly defined.

Use the drop-down lists in the **From Thermodynamics** column to match each species in the interface to a species in the coupled thermodynamic system.

For each species matched, the required property parameters and functions are added under to the corresponding thermodynamic system.

When all species are matched, the interface is considered fully coupled and functions representing mixture properties, such as density, are also added automatically under the corresponding thermodynamic system.

CALCULATE TRANSPORT PROPERTIES

Transport properties are not utilized in the reactor equations available in the Reaction Engineering interface, where perfect mixing is assumed. However, transport properties such as diffusivity, thermal conductivity, and viscosity are of central importance when solving time- and space-dependent models. The physics interface helps to set up detailed expressions of species transport properties and transfers them automatically to the multiphysics model through the Generate Space-Dependent Model feature.

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

Select the **Calculate mixture properties** check box to enable calculation of mixture transport properties exported from the Reaction Engineering interface.

From the list for each property, select the in-built **Automatic** expression or set a **User defined** entry. The mixture properties you can transfer for space-dependent models are:

- **Heat capacity** (c_p) (SI unit: J/(kg·K)) (this is available when the Energy Balance is set to **Include**)
- **Thermal conductivity** (k) (SI unit: W/(m·K))
- **Dynamic viscosity** (μ) (SI unit: Pa·s) (this is available when a Species Type is set to **Solvent**)
- **Mixture density** (ρ) (SI unit: kg/m^3) (this is available in the Mixture Properties section)

All species properties needed to compute the mixture properties are entered in the **Species Transport Expression** or **Species Thermodynamic Expression** in the Species node.

Transport Properties

EQUILIBRIUM SPECIES VECTOR

This section is available when at least one equilibrium reaction has been defined, i.e. when a Reaction node incorporates at least one **Equilibrium** reaction (**Reaction type** is set to **Equilibrium**), or when at least one equilibrium reaction has been defined in an Equilibrium Reaction Group.

In the **Predefined dependent species (separated by ',')** text field, edit, if necessary, the species that depends on the composition of the other species according to the **Equilibrium expression** in the Reaction node. To minimize the impact of any numerical errors, it is recommended to set the species with the highest concentration as dependent species. The default species is set to the leftmost species in the **Reaction formula**.

The **Suppress negative concentrations** check-box exists to aid the computation of equilibrium reaction systems. A selected check-box ensures that no negative values of concentrations are accepted as solution to the equilibrium condition.

Example II in Handling of Equilibrium Reactions.

ACTIVITY

Select the **Use activity** check box to solve for species activities instead of species concentrations, which is a common approach when non-ideal fluids are modeled.

An activity coefficient other than 1 can be set for each species for the Species node in the **Species Concentration/Activity** section.

Activity

CHEMKIN IMPORT FOR SPECIES PROPERTIES

This section enables CHEMKIN® import to simulate complex chemical reactions in gas phase.

Two types of CHEMKIN input files can be imported here — **Thermo** and **Transport,** for thermodynamic properties and transport properties respectively. Properties for either volumetric or surface species are supported. Click **Browse** to locate the CHEMKIN file to be imported, then click **Import**. For Thermo the imported data is directly entered in the **NASA format** fields in the Species **Thermodynamic Expressions** section. For Transport the imported data is entered in the Species **Transport Expressions** section.

- CHEMKIN Data and NASA Polynomials
- Reversible Reaction Group

ADVANCED SETTINGS

To display this section, click the **Show More Options** button ( ) and select **Advanced Physics Options**.

The **Uniform scaling of concentration variables** check box is not selected by default. When selected, all concentration variables are scaled using the same scale factor in the **Study** node. Enabling uniform scaling can decrease solver time for problems involving many concentration variables.

Features Nodes Available for the Reaction Engineering Interface

The following feature nodes are available from the **Reaction Engineering** ribbon toolbar (Windows users), **Reaction Engineering** context menu (Mac or Linux users), or right-click to access the context menu (all users).

- Initial Values
- Reaction
- Species
- Reversible Reaction Group
- Equilibrium Reaction Group
- Species Group
- Additional Source
- Reaction Thermodynamics[1]
- Species Activity[1]
- Species Thermodynamics[1]
- Feed Inlet
- Generate Space-Dependent Model
- Parameter Estimation[2]
- Experiment[2]

[1] This is a subnode and it is only available together with a parent node.

[2] Requires the addition of the Optimization Module.

Initial Values

The **Initial Values** node sets the initial values of the dependent variables solved for in the Reaction Engineering interface.

GENERAL PARAMETERS

For **CSTR, constant mass** and **Semi** reactor types, in which the reactor volume changes with reaction, an **Initial system volume** $Vr0$ can be set.

For nonisothermal conditions (that is, the Energy Balance is set to **Include**), enter an **Initial temperature** T_0 for the system. For the **Plug flow** reactor a corresponding **Inlet temperature** $T_{0,\text{in}}$ is entered.

VOLUMETRIC SPECIES INITIAL VALUE

In the **Volumetric species initial concentration** table, the **Species** column automatically includes all the species in the model. Enter the corresponding values or expression for each species initially in the **Concentration (mol/m^3)** column.

For the **Plug flow** reactor an **Inlet molar flow rate** table is instead shown. Enter the values or expressions representing the inlet conditions of each species in the **Molar flow rate (mol/s)** column.

SURFACE SPECIES INITIAL VALUE

The **Surface Species Initial Value** table is displayed when surface species are present in the reactor, i.e. when the Species Type is set to **Surface species** for at least one species in the reactor. Enter in the **Surface concentration (mol/m^2)** column, the corresponding values or expression for each species initially on the reactive surface area (A_r) within the reactor. The values in the **Site occupancy number** column are by default set to 1, edit the value if a surface species takes up more than one active site on the reactive surface.

The total surface concentration initially is always restricted by the molar amount of available sites on the reactive surface area. This is defined by the **Initial density of surface sites** γ_0 (SI unit: $\mathrm{mol/m^2}$) entry. Make sure that the sum of the entered initial surface concentrations do not surpass the value selected here. Note that the actual surface concentration of each species is the **Surface concentration (mol/m^2)** multiplied with the **Site occupancy number**. The restriction of the total surface concentration is defined as:

$$\gamma_0 \geq \sum_i c_{\mathrm{surf,\,i}} \cdot \mathrm{number}_{\mathrm{site\ occupancy,\,i}} \tag{2-82}$$

REACTOR AREA

This section is displayed when surface species are present in the model. Set the **Reactor area** — in other words, the total reactive surface area available in the reactor — here.

Reaction

To add a **Reaction** node ( ) either right-click the **Reaction Engineering** node or on the **Reaction Engineering** toolbar click **Reaction**.

REACTION FORMULA

Formula

Enter a chemical reaction **Formula**. Click **Apply** to make the interface examine the species taking part in the model's reactions and automatically add the associated Species features to the Model Builder.

Check stoichiometric balance

If all species are written using their chemical formula (e.g. "H2O" rather than "water"), this check box enforces balance checking. This ensures that the number of atoms of each kind are the same on both sides of the reaction. For example, the formula "H2+O2=>H2O" will trigger an error, while "8H2+4O2=>8H2O" will be accepted.

Balance ( )

If all species are written using their chemical formula, the stoichiometric coefficients can automatically be calculated, if the problem is well posed, by clicking the **Balance** button to the right of the **Reaction Formula** section title. This turns e.g. the formula "H2+O2=>H2O" into "2H2+O2=>2H2O".

Examples of problems that are not well posed are for example "C+H2=>CH4+C2H6", from which any ratio of CH_4/C_2H_6 could be obtained, and "H2=>O2", where not all elements are present on both sides.

Reaction Type

Select the **Reaction type** — **Reversible**, **Irreversible**, or **Equilibrium** — or edit the expression directly in the **Formula** field. In the latter case, specify the reaction type with a delimiter separating the two sides of the equation:

- <=> denotes a **Reversible** reaction
- => denotes an **Irreversible** reaction
- = denotes a reaction at chemical **Equilibrium**

Each **Reaction type** has its own set of reaction kinetics:

- If the reaction is **Reversible** or **Irreversible**, the reaction rate for reaction i contributes to the change in species i as follows:

$$R_i = \sum_j \nu_{ij} r_j \tag{2-83}$$

where ν_{ij} is the stoichiometric coefficient.

- If it is an **Equilibrium** reaction, the equilibrium expression is equal to the equilibrium constant:

$$K_{eq} = K_{eq0} \tag{2-84}$$

REACTION RATE

This section is available when the **Reaction type** is either **Reversible** or **Irreversible**.

When **Mass action law** is selected (default), the rate expression is automatically derived from the stoichiometric coefficients in the reaction formula:

- For an **Irreversible** reaction type, the reaction rate becomes:

$$r_j = k_j^f \prod_{i \in \text{react}} c_i^{-\nu_{ij}} \tag{2-85}$$

- For a **Reversible** reaction type, the expression instead becomes:

$$r_j = k_j^f \prod_{i \in \text{react}} c_i^{-\nu_{ij}} - k_j^r \prod_{i \in \text{prod}} c_i^{\nu_{ij}} \tag{2-86}$$

The deduced overall reaction order is shown in text below the respective equation in the **Reaction Rate** section.

Arbitrary rate expression

If the reaction order differs from the stoichiometric coefficients, or if an arbitrary rate expressions is applicable, change **Reaction Rate** to **User defined**. An expression field r appears with the default expression being that from the mass action law. Below this there are fields to set the reaction order. For a reversible reaction the reverse reaction order may be specified in addition to the forward one. The unit of the rate constant k (or frequency factor A in the case of Arrhenius behavior), is derived from the reaction order, in SI units: $(\text{m}^3/\text{mol})^{\alpha-1}/\text{s}$, where α equals the order with respect to volumetric specfies. When surface species are present — identified by their "(ads)" suffix — the unit is instead given by $\text{m}^{3\alpha+2\beta-2}/\text{mol}^{\alpha+\beta-1}/\text{s}$, where β is the order with respect to surface species.

Consider for example the reaction:

$$2\ S_2O_4^{2-} + H_2O \Rightarrow S_2O_3^{2-} + 2\ HSO_3^-$$

The automatically deduced reaction order is three, however, in the case that water is the solvent, the order should probably be two. This is specified as follows:

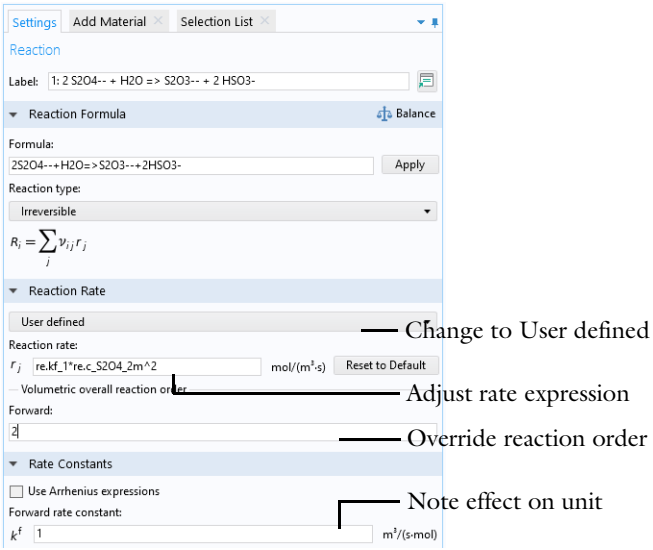


Figure 2-5: The reaction order can be manually specified for a user defined reaction rate.

RATE CONSTANTS

This section applies for **Reversible** or **Irreversible** reactions and defines the reaction rate constants used in the reaction rates.

Forward Rate Constant and Reverse Rate Constant

The **Forward rate constant** k^f is used for both **Reversible** and **Irreversible** reactions. The **Reverse rate constant** k^r is only used for **Reversible** reactions (Equation 2-86).

The SI units of the rate constants are automatically based on the order of the reaction with respect to the concentrations, as defined in the **Reaction formula**.

Specify Equilibrium Constant

The **Specify equilibrium constant** check box is available for **Reversible** reactions. If the check box is selected the rate constants are defined in a different manner with the reverse rate constant being computed from the following expression:

$$k^r = k^f / K_{eq0} \tag{2-87}$$

Thus, in this case, the forward rate constant and equilibrium constant for the reaction are needed. The **Equilibrium constant** is edited in the Equilibrium Settings section.

Use Arrhenius Expressions

When the **Use Arrhenius expressions** check box is selected the Arrhenius parameters are automatically used in predefined expressions for the forward and reverse rate constants k^f and k^r, respectively.

$$k^{\mathrm{f}} = A^{\mathrm{f}}(T/T_{\mathrm{ref}})^{n^{\mathrm{f}}}\exp(-E^{\mathrm{f}}/(R_{\mathrm{g}}T)) \tag{2-88}$$

$$k^{\mathrm{r}} = A^{\mathrm{r}}(T/T_{\mathrm{ref}})^{n^{\mathrm{r}}}\exp(-E^{\mathrm{r}}/(R_{\mathrm{g}}T)) \tag{2-89}$$

Specify the activation energy and the frequency factor in the Arrhenius expressions to account for temperature variations. The reference temperature, T_{ref} equals 1 K. The available fields are based on the **Reaction type** chosen in the Reaction node. Enter values or expressions for each of the following (reverse expressions are only available for reversible reactions):

- **Forward frequency factor** A^{f} and **Reverse frequency factor** A^{r} (unit depends on reaction order)
- **Forward temperature exponent** n^{f} and **Reverse temperature exponent** n^{r}
- **Forward activation energy** E^{f} and **Reverse activation energy** E^{r} (SI unit: J/mol)

EQUILIBRIUM SETTINGS

This section is available for equilibrium reactions, and for reversible reactions when the **Specify equilibrium constant** check box has been selected.

Equilibrium Expression

For an equilibrium reaction, specify the **Equilibrium expression**. When the **Equilibrium expression** is set to **Automatic** the following expression is used:

$$K_{\mathrm{eq}j} = \frac{\prod_{i \in \mathrm{prod}} c_i^{\nu_{ij}}}{\prod_{i \in \mathrm{react}} c_i^{-\nu_{ij}}} \tag{2-90}$$

Select **User defined** from the **Equilibrium expression** list to instead enter a manually defined equilibrium expression.

Equilibrium Constant

Specify the **Equilibrium constant** K_{eq0} for an equilibrium reaction, or for a reversible reaction when the **Specify equilibrium constant** check box has been selected (in the **Rate Constants** section).

The **Equilibrium constant** can either be **User defined**, or automatically defined when set to **Automatic** or **Thermodynamics**.

Use the **Automatic** option to compute the equilibrium constant for an ideal system. This setting requires that the temperature is also solved for by setting Energy Balance to **Included**.

The **Thermodynamics** option is available when all reactions in the interface are equilibrium reactions, and the interface is fully coupled to a Thermodynamic System (see Species Matching). Use this setting to automatically compute the equilibrium constant for an ideal or nonideal system, dependent on the thermodynamic model applied for the coupled system.

Using **Automatic** or **Thermodynamics**, K_{eq0} is calculated from the Gibbs free energy of the reaction. For more details see The Equilibrium Constant and the Automatically Defined Equilibrium Constants section therein.

REACTION THERMODYNAMIC PROPERTIES

This section contains information about thermodynamic properties that relate to a selected reaction and is available when the Energy Balance is set to **Include**. Several **Automatic** definitions are available here.

Enthalpy of Reaction

The **Enthalpy of reaction** H (SI unit: J/mol) is calculated by the interface from species properties and the related stoichiometric coefficients:

$$H_j = \sum_{i \in \text{prod}} \nu_{ij} h_i - \sum_{i \in \text{react}} (-\nu_{ij}) h_i \tag{2-91}$$

Entropy of Reaction

The **Entropy of reaction** S (SI unit: J/(mol·K)) comes from a similar expression:

$$S_j = \sum_{i \in \text{prod}} \nu_{ij} s_i - \sum_{i \in \text{react}} (-\nu_{ij}) s_i \tag{2-92}$$

In Equation 2-91 and Equation 2-92, h_i and s_i are the species' molar enthalpy and molar entropy, respectively.

Enter these quantities in the **Species Thermodynamic Expressions** section for the Species node either by using the predefined polynomial or by providing a custom expression or constants.

The stoichiometric coefficients ν_{ij}, are defined as being negative for reactants and positive for products. Using Equation 2-91 and Equation 2-92 to equate the Gibbs free energy of reaction enables the equilibrium constant to be expressed according to Handling of Equilibrium Reactions.

Heat Source of Reaction

The **Heat source of reaction** (SI unit: W/m^3) is automatically computed from the heat of each reaction j, given by:

$$Q_j = -r_j H_j$$

Using the Reaction Node

Species

When a Reaction is defined, a **Species** node ( ) is automatically generated for the participating reactants and products. This feature enables you to review and enter species specific information regarding chemical kinetics, thermodynamics and transport properties.

It is also possible to add and define an individual **Species** node: on the **Reaction Engineering** toolbar click **Species** or right-click the **Reaction Engineering** node and select it from the context menu.

SPECIES NAME

When a **Species** node is automatically generated using the **Formula** text field for the Reaction node, the **Species name** is also automatically generated.

For a **Species** node added individually, enter a **Species name** in the field and click **Apply**.

Creating Valid Species Names and Labeling

SPECIES TYPE

Select a species type — **Bulk species**, **Surface species**, or **Solvent**.

Bulk species and **Solvent** are solved for volumetric concentrations (SI unit: mol/m^3), while **Surface species** are solved for surface concentration (SI unit: mol/m^2). The compositions for **Bulk species** and **Solvent** use the syntax `c_speciesname`, while **Surface species** uses `csurf_speciesname_surf`.

Surface species is referring to species adsorbed on a reactive surface. When **Surface species** is selected, the corresponding reaction formula introduces **(ads)** after the species notation and changes the species' name to `speciesname_surf`. Additionally, the Species node name is updated in a similar fashion.

For the **Plug flow** reactor only **Bulk species** and **Solvent** are allowed.

Choosing the Species Type

GENERAL PARAMETERS

The **General Parameters** section deals with species parameters.

The default value for the **Molar mass**, M (only shown when needed), and the ionic **Charge**, z, of the species is automatically defined from the species name by assuming that it corresponds to its chemical formula. Provided that the formula contains elements from the periodic table, the species molar mass is computed from mass the of occurring individual elements[1]. When the species name contains parts not in the periodic table, for example when a descriptive name such as `water` is used, the molar mass is set to 0.0 kg/mol and the charge to zero. In this case, the molar mass needs to be defined in order to achieve mass balanced reactions and correct definitions of mass basis properties. The species charge is also deduced from the species name. Creating a `H+` species, the charge will be set to one. When needed, both the **Molar mass** and the **Charge** can be edited in the corresponding edit field.

It is possible to specify the species density ρ when the fluid **Mixture** is specified as **Liquid**. The default value is that of water at 293 K.

1. Values are averages of upper and lower bounds for each atom as published by CIAAW. Source: CIAAW. Atomic weights of the elements 2019. Available online at www.ciaaw.org.

REACTION RATE

Change the **Automatic** default setting to **User defined** to use a species reaction rate other than the one set up in the associated Reaction node. For individual species, use the **User defined** option to set a reaction rate other than zero (that is, nonreactive).

Edit either the **Rate expression** (SI unit: mol/(m^3s)), the **Surface rate expression** (SI unit: mol/(m^2s)), or both. For a bulk species, both expressions appear if surface reactions are present in the reactor since the reaction of the species can depend both on bulk reaction R and surface reaction R_{ads} rates. For a surface species, only the surface reaction rate R_{ads} appears.

The reaction rate is not editable if the species in question participates in an equilibrium reaction and has been selected as a **Predefined dependent species** in Calculate Transport Properties.

SPECIES CONCENTRATION/ACTIVITY

To account for nonideality in the fluid mixture adjust the activity coefficient in the **Activity coefficient** text field here. The section is only shown if activity instead of concentration has been chosen in the interface; that is, the **Use activities** check box is selected on the Reaction Engineering interface **Settings** window

Click to select the **Constant concentration/activity** check box if the species concentration or activity should be treated as constant.

SPECIES TRANSPORT EXPRESSIONS

Here the required parameters to compute various transport properties can be edited. To show this section the **Calculate mixture properties** check box needs to be selected under the **Calculate Transport Properties** section.

- For a gas mixture, there are maximum five properties to consider:
  - σ, the characteristic length (unit: Å) of the Lennard-Jones/Stockmayer potential
  - ε/k_b (SI unit: K) the potential energy minimum value of the of the Lennard-Jones/Stockmayer potential, divided by Boltzmann's constant. Tabulated data in literature frequently lists values of ε/k_b rather than ε
  - μ_D, the dipole moment (SI unit: Debye)
  - k_i, the thermal conductivity of the gas (SI unit: W/(m K)); and Diffusivity of the species (SI unit: m^2/s). The latter two can be set to **Automatic**, when σ and ε/k_b have been given.
- For mixtures of gas with solvent, all properties above except the thermal conductivity is shown. This is instead calculated under the **Calculate mixture properties** section on the Settings window for the Reaction Engineering interface. This requires that Energy Balance is set to **Included**.
- For a liquid mixture, there is only the parameter k_i, the thermal conductivity (SI unit: W/(m K)) to edit.
- For mixtures of liquid with solvent, the thermal conductivity is shown only for the species set as **Solvent**.

SPECIES THERMODYNAMIC EXPRESSIONS

The parameters utilized for calculation of thermodynamic mixture and reaction properties are set in this section. It is accessed when the Energy Balance is set to **Include** for the Reaction Engineering interface, in other words for nonisothermal conditions.

The **Species Thermodynamic Expressions** are by default computed using data in the **NASA format**. In this case, enter the following to compute the species' heat capacity, C_p (SI unit: J/(mol·K)), the molar enthalpy, h (SI unit: J/mol), and the molar entropy, s (SI unit: J/(mol·K)):

- **Lower temperature limit** T_lo
- **Middle temperature limit** T_mid
- **Upper temperature limit** T_hi
- **Polynomial coefficients** $a_{\mathrm{low},k}$ and $a_{\mathrm{hi},k}$

Any coefficients for the thermodynamic polynomials entered into the $a_{\text{low},k}$ fields apply to the temperatures in the range T_{lo} to T_{mid}; coefficients entered into the $a_{\text{hi},k}$ fields apply to temperatures in the range T_{mid} to T_{hi} range. The coefficients can also be imported in the **CHEMKIN Import for Species Properties** section in the Reaction Engineering node.

Choose the **User defined** alternative to specify C_{p}, h, and s directly.

Using the Species Node

Transport Properties

Reversible Reaction Group

The **Reversible Reaction Group** node ( ) allows input of a large number of reversible reactions in the same table. All reactions are treated in the same way. More than one Reversible Reaction Group can be added to a component. The feature is typically used when importing CHEMKIN kinetics files.

Add the node from the **Reaction Engineering** toolbar or right-click **Reaction Engineering** and add it from the context menu.

For the case when reaction kinetics data are entered manually into the **Reaction table** and nonisothermal conditions apply (Energy Balance is set to **Include**), right-click to add a Reaction Thermodynamics subnode or select it from the **Reaction Engineering** toolbar, **Attributes** menu. In it, the Enthalpy of Reaction (J/mol) for each reaction can be specified.

REACTION TABLE

The reversible reactions in the **Reaction table** are numbered and contain reactants, products, and kinetic parameters describing the reaction. Use the buttons under the **Reaction table** to add and sort the reaction details.

- In general, use the **Move Up** ( ), **Move Down** ( ), and **Delete** ( ) buttons and the fields under tables to edit the table contents. Or right-click a table cell and select **Move Up**, **Move Down**, or **Delete**.
- The **Add** button ( ) adds default reactant, A, and product, B, with a default. Click the corresponding field to edit the reactant, product, or parameters. After editing the Species Group node is also updated. It is created together with the reaction group.

- You can save the parameters to a text file to reuse in other models. Click the **Save to File** button ( ) and enter a **File name** in the **Save to File** dialog box, including the extension `.txt`. Click **Save** to store the parameters in a text file or in a Microsoft Excel Workbook spreadsheet if the license includes LiveLink™ *for* Excel®. The information is saved in space-separated columns in the same order as displayed on screen. When saving to Excel, an **Excel Save** dialog box appears where you can specify the sheet and range and whether to overwrite existing data, include a header, or use a separate column for units.
- You can import or load data in files from a spreadsheet program, for example, with the **Load from File** button ( ) and the **Load from File** dialog box that appears. Data must be separated by spaces or tabs. If there is already data in the table, imported parameters are added after the last row. Move or edit rows as needed. If the license includes LiveLink™ *for* Excel® you can also load parameters from a Microsoft Excel Workbook spreadsheet. Then an **Excel Load** dialog box appears where you can specify the sheet and range and whether to overwrite existing data. It is also possible to import from a spreadsheet containing a separate column for units.

CHEMKIN IMPORT FOR KINETICS

Click to select the **Import CHEMKIN data** check box to import a CHEMKIN **Kinetics input file**. To import the data directly into the table columns, click **Browse** to locate the CHEMKIN file to be imported, then click **Import**.

CHEMKIN Data and NASA Polynomials

MOVE REACTION AND SPECIES

Enter a reaction number in the **Moving reaction (with the number) from table** text field and click **Create Reaction** to remove the reaction from the **Reaction table** to the model tree. This introduces a reaction node named after the reaction number and species names and simultaneously creates corresponding species nodes. This action is powerful, since it enables all the editing possibilities available for Reaction and Species nodes.

Equilibrium Reaction Group

The **Equilibrium Reaction Group** node ( ) allows for input of a large number of equilibrium reactions in the same table. This node functions in the same way as the Reversible Reaction Group for reversible reactions.

Add the node from the **Reaction Engineering** toolbar or right-click **Reaction Engineering** and add it from the context menu.

For the case when reaction kinetics data are entered manually into the **Reaction table** and nonisothermal conditions apply (Energy Balance is set to **Include**), right-click to add a Reaction Thermodynamics subnode or select it from the **Reaction Engineering** toolbar, **Attributes** menu. In it, the Enthalpy of Reaction (J/mol) for each reaction can be specified.

EQUILIBRIUM REACTION TABLE

The equilibrium reactions in the **Reaction table** are numbered and contain reactants, products, and kinetic parameters describing the reaction. Use the buttons under the **Reaction table** to add and sort the reaction details.

- In general, use the **Move Up** ( ), **Move Down** ( ), and **Delete** ( ) buttons and the fields under tables to edit the table contents. Or right-click a table cell and select **Move Up**, **Move Down**, or **Delete**.
- The **Add** button ( ) adds default reactant, A, and product, B, with a default. Click the corresponding field to edit the reactant, product, or parameters. After editing the Species Group node is also updated. It is created together with the reaction group.
- You can save the parameters to a text file to reuse in other models. Click the **Save to File** button ( ) and enter a **File name** in the **Save to File** dialog box, including the extension `.txt`. Click **Save** to store the parameters in a text file or in a Microsoft Excel Workbook spreadsheet if the license includes LiveLink™ *for* Excel®. The information is saved in space-separated columns in the same order as displayed on screen. When saving to Excel, an **Excel Save** dialog box appears where you can specify the sheet and range and whether to overwrite existing data, include a header, or use a separate column for units.
- You can import or load data in files from a spreadsheet program, for example, with the **Load from File** button ( ) and the **Load from File** dialog box that appears. Data must be separated by spaces or tabs. If there is already data in the table, imported parameters are added after the last row. Move or edit rows as needed. If the license includes LiveLink™ *for* Excel® you can also load parameters from a Microsoft Excel

Workbook spreadsheet. Then an **Excel Load** dialog box appears where you can specify the sheet and range and whether to overwrite existing data. It is also possible to import from a spreadsheet containing a separate column for units.

In the case of twenty or more reactions the **Disable updating variables during editing table** check box is available. Select this to speed up editing text fields; automatic updates related to edits do not occur until you click to clear the check box.

MOVE REACTION AND SPECIES

Enter a reaction number in the **Moving reaction (with the number) from table** text field and click **Create Reaction** to remove the reaction from the **Reaction table** to the model tree. This introduces a reaction node named after the reaction number and species names and simultaneously creates corresponding species nodes. This action is powerful, since it enables all the editing possibilities available for Reaction and Species nodes.

Homogeneous Charge Compression Ignition of Methane: Application Library path **Chemical_Reaction_Engineering_Module/Ideal_Tank_Reactors/compression_ignition**

Chemical Vapor Deposition of GaAs: Application Library path **Chemical_Reaction_Engineering_Module/Reactors_with_Mass_and_Heat_Transfer/gaas_cvd**

Species Group

The **Species Group** node ( ) contains information on a molecular level about the volumetric species and the surface species present in the model. The **Property for Volumetric Species** or **Property for Surface Species** tables typically collect parameters from when importing CHEMKIN transport files.

Add the node from the **Reaction Engineering** toolbar or right-click **Reaction Engineering** and add it from the context menu. This node is also automatically added when either the Reversible Reaction Group or the Equilibrium Reaction Group are used.

For the case of nonisothermal reactor conditions (Energy Balance is set to **Include**), a Species Thermodynamics subnode is automatically created in which the thermodynamic properties of the species can be specified.

CHEMKIN

This section allows import of CHEMKIN transport files. To import the data directly into the table columns, click **Browse** to locate the CHEMKIN file to be imported, then click **Import**. Note that this section is only shown when transport properties are computed (**Calculate mixture properties** check box under the **Calculate Transport Properties** is selected).

CHEMKIN Data and NASA Polynomials

Additional Source

Use the **Additional Source** node ( ) to add an additional rate expression (SI unit: mol/m^3) and/or an additional volumetric production rate (SI unit: m^3/s) to the mass balance of certain species.

Add the node from the **Reaction Engineering** toolbar or right-click **Reaction Engineering** and add it from the context menu.

ADDITIONAL VOLUMETRIC PRODUCTION RATE

An additional **Additional volumetric production rate** can be added for some of the available reactor types, namely **CSTR, constant mass/generic**, **CSTR, constant volume**, or **Semi**.

ADDITIONAL RATE EXPRESSION

Here, values or expressions describing additional rates can be entered for selected **Species** in the column denoted **Additional rate expression (mol/m^3*s)** within the **Volumetric species** table.

ADDITIONAL SURFACE SPECIES RATE

Here, values or expressions describing additional surface species rates can be entered for selected **Surface species** in the column denoted **Additional rate expression (mol/m^2*s)** within the **Surface species** table.

Reaction Thermodynamics

In the **Reaction Thermodynamics** subnode ( ), the Enthalpy of Reaction (SI unit: J/mol) of each reaction can be specified. This node overrides all the automatically calculated reaction enthalpies as defined in the Species Thermodynamics subnode.

Add the **Reaction Thermodynamics** node from the **Reaction Engineering** toolbar, **Attributes** menu. Alternatively, when the Energy Balance is set to **Include**, right-click a Reversible Reaction Group or Equilibrium Reaction Group and select it from the context menu.

Species Activity

The **Species Activity** subnode (ai) creates variables for the activities for all the species/surface species present in the Species Group parent feature. Edit the **Activity coefficient** field in the **Species Activity** or **Surface Species Activity** tables by clicking in these.

Species Activity is a subnode to the Species Group node. It is automatically generated when nonideality in the fluid mixture is accounted for; when the **Use activity** check box is selected in the **Activity** section.

Species Thermodynamics

The **Species Thermodynamics** node ( ) creates variables for the enthalpies, entropies, and heat capacities for all the species/surface species present in the Species Group parent feature. The purpose is to compute thermodynamic mixture properties and the heat of reactions.

This node is a subnode to the Species Group node when the Energy Balance is set to **Include**.

SPECIES THERMODYNAMICS PROPERTY

Select a **Type selection** for the thermodynamic properties. The **NASA format** alternative requires the setting of several polynomial constants and is typically used together with CHEMKIN import. The **User defined** alternative only requires input of Species molar enthalpy (SI unit: J/mol) and Species molar capacity (SI unit: J/(mol*K)).

CHEMKIN IMPORT FOR THERMODYNAMIC DATA

This section allows import of thermodynamic CHEMKIN transport files. To import the data directly into the table columns, click **Browse** to locate the CHEMKIN file to

be imported, then click **Import**. Note that this can only be done for the **NASA format** option.

- CHEMKIN Data and NASA Polynomials

Feed Inlet

The **Feed Inlet** ( ) feature is used for adding inlet streams to the reactor.

After adding a Reaction node and setting its Reactor to **CSTR, constant volume**, **CSTR, constant mass/generic**, or **Semi**, add a **Feed Inlet** node from the **Reaction Engineering** toolbar or right-click the **Reaction Engineering** node to add it from the context menu.

FEED INLET PROPERTIES

Edit the **Volumetric feed rate** (v_f) (SI unit: m^3/s) to fit the modeling conditions.

The **Feed inlet temperature** (T_f) is required as input when nonisothermal conditions are investigated (Energy Balance is set to **Include**).

FEED STREAM CONCENTRATION

For each of the Species, enter a value or expression in the table for the **Concentration (mol/m^3)** to set the composition of the inlet stream.

FEED STREAM CONCENTRATION AND ENTHALPY

For each of the Species, enter values or expressions in the table for the **Concentration (mol/m^3)** and **Enthalpy (J/mol)** to set both the composition and enthalpy of the feed inlet stream. Note that in the rightmost column of the **Feed inlet concentration and enthalpy** table, it is possible to select that the thermodynamic properties are taken from a Species node instead.

- CSTR, Constant Mass/Generic
- CSTR, Constant Volume
- Semibatch

Generate Space-Dependent Model

It is often relevant to perform an extended analysis of the reaction model. For example, to study how a reacting system's detailed geometry impacts the concentration and temperature distributions. Use the **Generate Space-Dependent Model** feature tool to export the properties within the Reaction Engineering interface to other COMSOL Multiphysics interfaces where a space-dependent model is set up. Properties that are exported are reaction kinetics, thermodynamics, and transport parameters.

To add this feature, on the **Reaction Engineering** toolbar click **Generate Space-Dependent Model** ( ) or right-click the **Reaction Engineering** node to add it from the context menu. Only one **Generate Space-Dependent Model** node can be added per model file.

SELECTING THE MODEL GENERATION SETTINGS

To utilize the **Generate Space-Dependent Model** feature, make selections in the following order:

1. Select the component to use: 1D Axisymmetric, 1D, 2D, 2D Axisymmetric, 3D, or an existing component within the model builder.
2. Select the physics interfaces.
3. Select a study type.

Then click the **Create/refresh** button to create the space-dependent model (Figure 2-6).

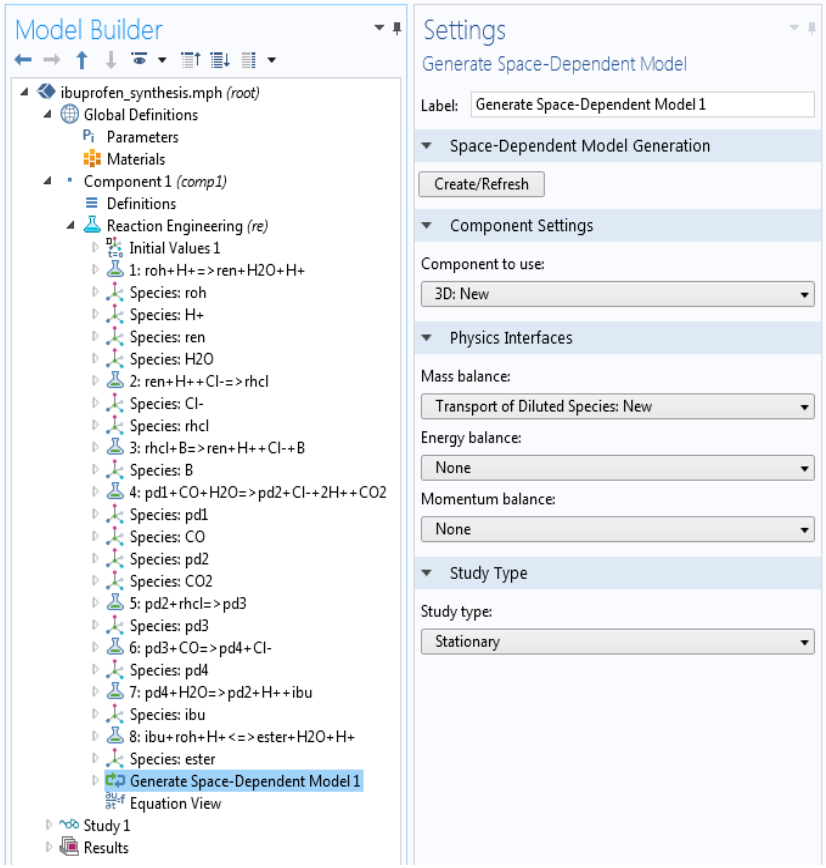


Figure 2-6: The Generate Space-Dependent Model transfers the properties from the Reaction Engineering interface to physics interfaces in a1D Axisymmetric, 1D, 2D, 2D Axisymmetric, or 3D component.

If more interfaces are needed in a component after the initial model generation, select the component and the new interface(s) and click **Create/refresh** to introduce the interface into it.

COMPONENT SETTINGS

Select a **Component to use**. Either specify the space dimension of a new component — **1D**, **1Daxi**, **2D**, **2Daxi**, and **3D** — or select a component already defined in the Model Builder.

PHYSICS INTERFACES

Select the applicable physics interfaces to create or update from the **Chemical species transport**, **Fluid flow**, and **Heat transfer** lists. The physics interfaces available are based on the specific modules installed. These include the Chemical Reaction Engineering Module, the MEMS Module, the Heat Transfer Module, and the Subsurface Flow Module. Note that a mass balance physics interface must always be selected when generating a space-dependent model.

If desired, physics interfaces for fluid flow, heat transfer, or other features affecting the reacting system can be added later separately from the physics interfaces created by the **Generate Space-Dependent Model** feature.

The Chemistry Interface is always created and added when generating a space-dependent model. It generates and announces global variables for the reaction kinetics, thermodynamics, and transport properties from the Reaction Engineering interface. The global variables generated are available for all space-dependent interfaces. Figure 2-7 displays an application where a Reactions feature uses reaction rates defined by a Chemistry interface. The syntax `chem` points to the default **Name** of the Chemistry node.

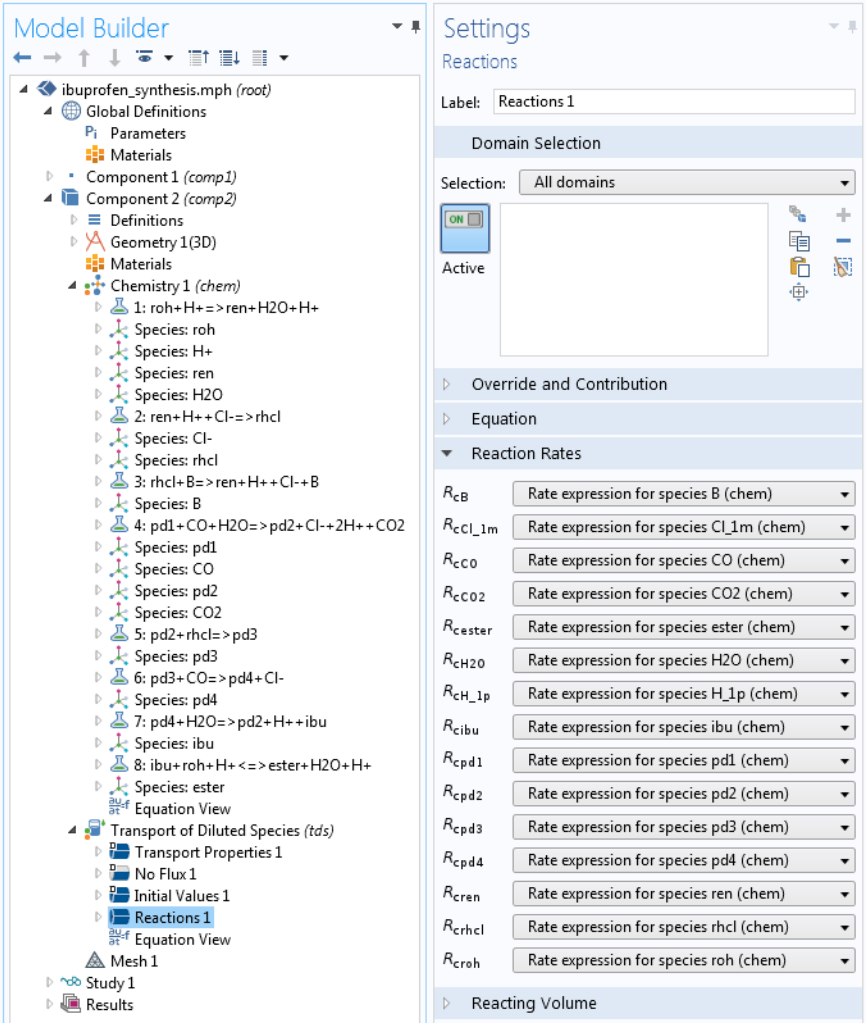


Figure 2-7: The Chemistry node generates global variables from rate variables and properties defined in the Reaction Engineering interfaces, and announces these to be used in relevant sections of other generated space-dependent interfaces. The Reaction Rates within a Reactions feature in a Transport of Dilute Species interface illustrate this.

If necessary, variables and properties in the Chemistry node can be accessed with the Chemistry node **Name** (default `Chem`). An arbitrary reaction rate expression, R, is thus written as `comp2.chem.R` in the corresponding text fields of the generated interface (see Figure 2-7).

When surface species are present (that is, when the Species Type is set to **Surface species** for at least one species in the reactor), specify how to include surface reactions in the space-dependent model.

From the **Surface reaction on** list, select **Boundaries** or **Porous Pellets**.

- When **Boundaries** is selected, the surface reactions will be modeled using a **Surface Reactions** interface defined on the boundaries of the geometry.
- When **Porous Pellets** is selected, the surface reactions will be modeled using a **Reactive Pellet Bed** feature added to a **Transport of Diluted Species** interface or a **Diluted Species in Porous Media** interface. In this case the content of the **Mass balance** list is restricted to these interfaces.

A corresponding reaction feature is added and set up, in accordance with the reaction kinetics defined in the **Reaction Engineering** interface, when clicking the **Create/Refresh** button in the **Space-Dependent Model Generation** section. In Figure 2-8, the surface reaction kinetics in a **Reacting Engineering** interface has been implemented in a **Reactive Pellet Bed** feature using a **Reactions** subfeature. Note that the surface reaction rates are defined by the **Chemistry** interface.

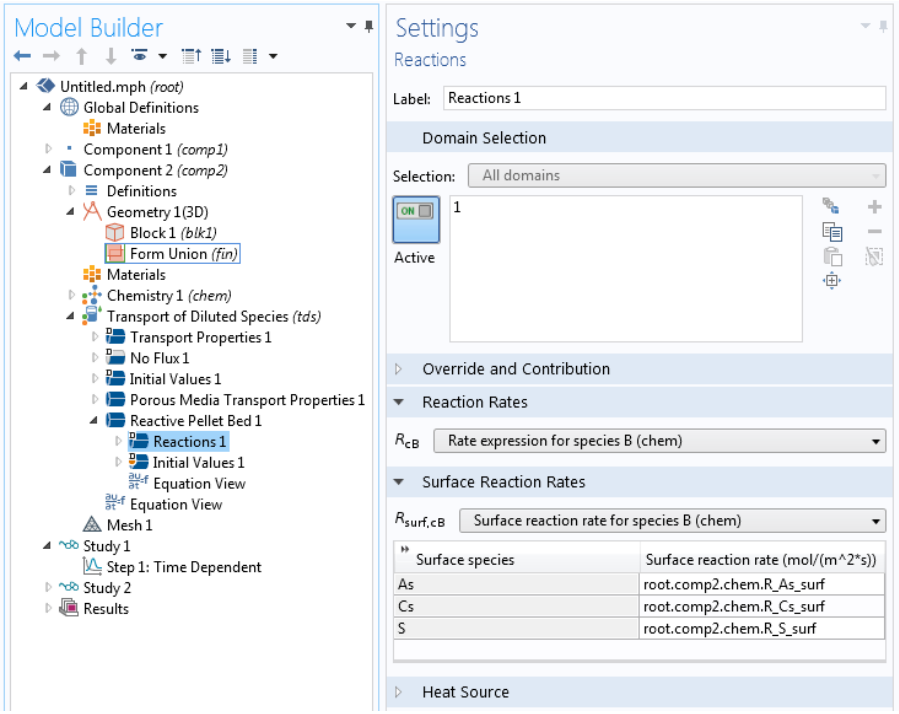


Figure 2-8: A Reactive Pellet Bed feature with a Reactions subfeature can be automatically created, using a Generate Space-Dependent Model feature, from a Reaction Engineering interface containing surface species.

- Theory for the Reactive Pellet Bed
- The Transport of Diluted Species Interface

Chemical Species Transport

The following Chemical Species Transport interfaces are available with the Chemical Reaction Engineering Module:

- The Transport of Diluted Species Interface
- The Transport of Diluted Species in Porous Media Interface
- The Nernst–Planck Equations Interface
- The Transport of Concentrated Species Interface

The model generation automatically defines the dependent variables for all species. The Transport of Diluted Species, Nernst-Planck Equations, and Transport of Diluted Species in Porous Media interfaces use the default variable names according to the syntax `cspeciesname`, referring to species concentrations in mole per volume. The Transport of Concentrated Species interface uses the syntax `wspeciesname` for default variable names, referring to the species weight fraction. The initial values for the dependent species variables in the space-dependent model, are based on the initial species values collected in the Reaction Engineering interface. Note that only the Transport of Diluted interface is available for systems with equilibrium reactions.

Binary diffusion coefficients of different kinds can be computed and transferred to a space-dependent model. The available diffusion models for the mass balance physics interfaces sometimes require the binary diffusion coefficients of the mixture, describing all pairwise diffusion interactions between species. Under the assumption of an ideal gas the Transport of Concentrated Species interface can utilize the binary diffusion coefficient. The Transport of Diluted Species and Nernst-Planck Equations interfaces assumes that the chemical species being transported are present in small amounts and are diluted in a solvent. The binary diffusion coefficient in these cases (in the presence of a solvent species) become the diffusion coefficient of the bulk species.

Heat Transfer

The Reaction Engineering interface can also be set up with time- and space-dependent energy balance equations. In the model generation process the physics interface generates expressions used by the Heat Transfer interface, such as the heat generated by a chemical reaction. It also generates expressions for physical transport properties.

There are two heat transfer interfaces under the Energy balance:

- Heat Transfer in Fluids
- Heat Transfer in Porous Media

Several expressions for the species density, heat capacity, and thermal conductivity are available and can be transferred from the Reaction Engineering interface.

The densities are available from the Equilibrium Species Vector section in the interface, where the fluid mixture properties are selected. The density depends on the Species settings and is computed as follows for:

- Liquid, if assuming the liquid to be ideal and incompressible. The liquid mixture density depends on the density of i number of pure species, ρ_i, and the species weight fraction, w_i.

$$\rho = \frac{1}{\sum_i \frac{w_i}{\rho_i}} \tag{2-93}$$

The volume fraction is given by the species concentration, c_i, and the molar mass, M_i.

$$w_i = \frac{c_i M_i}{\sum_i c_i M_i} \tag{2-94}$$

- Gas mixture density depends on the concentrations and molar masses of the mixture species.

$$\rho = \sum_i c_i M_i \tag{2-95}$$

For mixtures with solvent all values are taken from the species set as solvent.

The heat capacity, c_p (SI unit: J/(mol·kg)), of the mixture is calculated by the species' molar heat capacity, C_p (SI unit: J/(mol·kg)) according to

$$c_p = \sum_i w_i \frac{C_{p,i}}{M_i} \tag{2-96}$$

where M is the molar mass (SI unit: kg/mol) and w_i the weight fraction.

Fluid Flow

The model generation process can be selected to generate a Fluid Flow interface.

There are these separate momentum balance physics interfaces:

- The Single-Phase Flow, Laminar Flow Interface
- The Darcy's Law Interface (in the *CFD Module User's Guide*)
- The Free and Porous Media Flow Interface (in the *CFD Module User's Guide*)

Species density (see Equation 2-93, Equation 2-94, and Equation 2-95) and dynamic viscosity can for some mixture options be transferred from the Reaction Engineering interface to the Fluid Flow interfaces.

Transport Properties

	NOx Reduction in a Monolithic Reactor: Application Library path **Chemical_Reaction_Engineering_Module/Tutorials/monolith_3d** *Hydrocarbon Dehalogenation in a Tortuous Microreactor*: Application Library path **Chemical_Reaction_Engineering_Module/Reactors_with_Mass_Transfer/tortuous_reactor** *Protein Adsorption*: Application Library path **Chemical_Reaction_Engineering_Module/Mixing_and_Separation/protein_adsorption**

STUDY TYPE

Select a **Study Type**, either **Stationary** or **Time Dependent**. It is also possible to edit this choice after the space-dependent model has been generated.

Parameter Estimation

The **Parameter Estimation** feature ( ) requires the Optimization Module.

Add the node from the **Reaction Engineering** toolbar or right-click **Reaction Engineering** and add it from the context menu. The node and related subnodes have the options and settings for the definition of parameter estimation calculations based on the predefined reactor types in the Reaction Engineering interface.

ESTIMATION PARAMETERS

The parameters to be estimated are defined in the **Estimation parameters** table. The parameter names are entered in the **Parameter** column. An **Initial value** is also required for each variable. To connect the estimated parameters to the model, make sure that the same parameter naming is used within the rest of the Reaction Engineering interface.

Bounds for the parameter values are specified in the **Lower bound** and **Upper bound** columns of the **Estimation parameters** table. These are applicable when the SNOPT optimization (Solver Study Steps for Parameter Estimation) solver method is used. The default solver method for parameter estimation is Levenberg-Marquardt, which currently does not support parameter bounds. Enter a **Scale** indicating a typical magnitude of the control variable. The relative solver tolerances refer to variables rescaled with respect to this scale, and it may also influence the search pattern of some optimization solvers.

Experiment

The **Experiment** node organizes the data and the conditions for a particular experiment. This is also where experimental variables are associated with model variables in order to set up the parameter estimation.

Right-click the Parameter Estimation node to add one or more **Experiment** nodes. You can also select it from the **Reaction Engineering** toolbar, **Attributes** menu, enabled when the Parameter Estimation node is selected.

Notice that the **Experiment** node requires the Optimization Module.

EXPERIMENTAL DATA

Experimental data is read into the software by importing comma-separated value files, *CSV files*. After import, identifiers display in the **Data column** of the **Experimental Data** table (Figure 2-9). If the CSV files have column headers, these are used to identify the columns. If the data file does not have column headers, the columns are identified by a number. It is assumed that the first column corresponds to the independent variable for time (t). In the **Model variables** column, the measured data is correlated with model variables by entering the proper variable names or expressions. The **Use** column controls whether to include data in the parameter estimation calculation or not. Data column entries require associated **Model variables** to be accounted for the parameter estimation calculations.

In the **Unit** column, enter the unit of the imported experimental data.

In the **Weight** column, enter a strictly positive value. The difference between the value of the **Model variable** and the **Data column** value is squared and multiplied with the **Weight** and a factor 0.5 to give the contribution to the total objective for each measured value.

Imported data can be inspected in the corresponding **Table** node located under the **Results** branch (Figure 2-9). An **Experiment Table** is created each time the **Import** button is clicked.

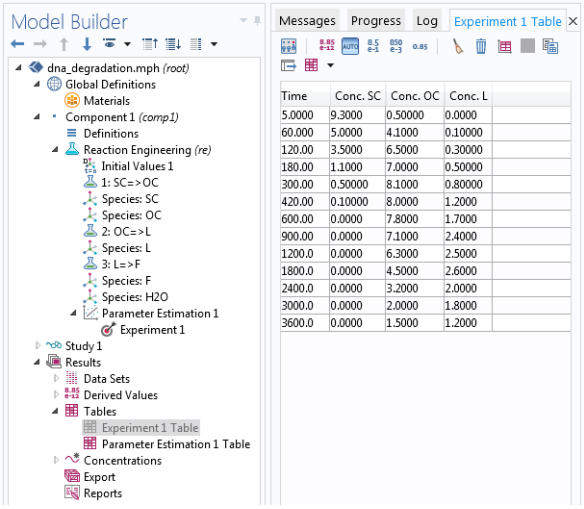


Figure 2-9: The content of imported data files is presented in a Table.

EXPERIMENTAL PARAMETERS

Each **Experiment** node can be associated with user-defined parameters during the parameter estimation. For example, concentration transients can be measured for a number of different isothermal conditions. **Parameter name** and **Parameter expression** are added from a list. The list is populated with the parameters that are defined in the Parameters under Global Definitions in the Model Builder.

INITIAL STATES

A given experiment usually determines the initial values for the dependent variables in the reactor model, such as the initial concentrations for isothermal reactor models and initial concentrations and temperature for nonisothermal reactor models.

Initial conditions that change from one experiment to another need to be provided in the **Initial States** section of the Experiment node. An entry in the **Parameter names** column is added by choosing from a list of predefined variable names corresponding to the initial state of the reactor model.

Degradation of DNA in Plasma:
Chemical_Reaction_Engineering_Module/Ideal_Tank_Reactors/dna_degradation

Finding Kinetic Arrhenius Parameters Using Parameter Estimation:
Chemical_Reaction_Engineering_Module/Tutorials/activation_energy

- Solver Study Steps for Parameter Estimation
- www.comsol.com/optimization-module

The Chemistry Interface

This physics interface can be used to create reaction kinetics and optionally compute transport and thermodynamic properties for direct use in 1D, 2D, or 3D models. This is similar to The Reaction Engineering Interface, except that it does not solve for an ideal reactor model.

The **Chemistry (chem)** interface ( ) is found under the **Chemical Species Transport** branch ( ) when adding a physics interface. The Chemistry interface is also created when the Generate Space-Dependent Model feature is used in the Reaction Engineering interface, collecting all mixture variables and properties for use in a space-dependent model.

This physics interface is a tool for generating a set of variables to be used for modeling chemical species and reactions systems. The variables are generated from species and reaction properties and can be divided in two categories:

- Rate expressions and heat sources for use in mass and heat balances.
- Material property variables (mixture density, diffusivities, viscosity, and so on) for use in space-dependent transport equations.

Many of the fields and nodes described in this section are only made available when either a Reaction or a Species (or both) subnode is added to the Model Builder. All predefined constants and expressions can be overwritten by user-defined expressions. This makes it possible to go beyond the modeling assumptions set as defaults in this physics interface.

- Theory for the Reaction Engineering and Chemistry Interfaces
- Transport Properties
- Feature Nodes Available for the Chemistry Interface

The following is a description of the features and fields available on the **Settings** window for the Chemistry interface.

SETTINGS

The **Label** is the default physics interface name.

The **Name** is used primarily as a scope prefix for variables defined by the physics interface. Refer to such physics interface variables in expressions using the pattern

<name>.<variable_name>. In order to distinguish between variables belonging to different physics interfaces, the name string must be unique. Only letters, numbers, and underscores (_) are permitted in the **Name** field. The first character must be a letter.

The default **Name** (for the first physics interface in the model) is chem.

MODEL INPUT

This section sets the **Temperature, Pressure** and **Electrode potential** (only available with a Battery Design Module, Corrosion Module, Electrochemistry Module, Electrodeposition Module, or Fuel Cell & Electrolyzer Module license) to be used by the current interface. Use the lists to select a temperature, pressure or electrode potential defined and announced by another interface in the model. For example, when a heat transfer interface is also included, the temperature solved for is available in the **Temperature** list.

For **Temperature** or **Pressure**, you can also select **Common model input** to use a globally available common model input. In all three cases, select **User defined** to manually define the variable in question.

MIXTURE PROPERTIES

Type

Select **Diluted species** from the **Type** list to use the concentration variables from a Transport of Diluted Species interface in the Species Matching section. The same setting should be used for any other interface solving for species concentrations using a diluted species assumption. Select **Concentrated species** from the **Type** list to use the mass fractions from a Transport of Concentrated Species interface.

Thermodynamics

All property parameters and property functions required by the interface can be automatically created by coupling to a system added to the **Thermodynamics** node. To do so, click the **Thermodynamics** check box and select an existing Thermodynamic System.

The **Thermodynamics** check box is enabled when the Thermodynamics node, including one or more systems, is available under **Global Definitions**. Also, the Chemistry interface needs to include at least one species.

Phase

Use the **Phase** list to specify the state of aggregation of the mixture.

The mixture density settings are only available when you have selected the **Calculate mixture properties** check box in the **Calculate Transport Properties** section.

Density always has two settings available: **Automatic** or **User defined**. The **Thermodynamics** options is available when the interface is coupled to a Thermodynamic System, and all interface species has been matched to species in the system. In this case the density is defined by a function automatically added under the thermodynamic system coupled to.

The **Automatic** setting uses the following logic:

- When **Phase** is set to **Liquid**, **Automatic** assumes that the liquid is ideal and incompressible. The liquid mixture density depends on the density of i number of pure species (ρ_i) and the species weight fraction (w_i).

$$\rho = \frac{1}{\sum_i \frac{w_i}{\rho_i}}$$

  The volume fraction is given by the species concentration (c_i) and the molar mass (M_i).

$$w_i = \frac{c_i M_i}{\sum_i c_i M_i}$$

- When **Phase** is set to **Gas**, **Automatic** calculates the gas mixture density (ρ) from the concentrations (c_i) and molar masses (M_i) of the mixture species, which are automatically taken from Species features.

$$\rho = \sum_i c_i M_i \tag{2-97}$$

- If the Species Type, for one of the present species, is set to **Solvent,** and the **Mixture** is **Liquid**, the mixture density is the same as the solvent density. The species density is defined in the **General parameters** section of the corresponding Species node. When **Mixture** is **Gas**, the mixture density is calculated from Equation 2-97 only for the species set as **Solvent**.

SPECIES MATCHING

Species Concentration Input Table

Use the **Species concentration input** table to specify the concentrations to be used as arguments in variables generated by the Reaction and the Species features (the reaction rate for example). The species concentrations are also used in the mixture properties (transport and thermodynamic properties).

When **Diluted species** is selected in the **Type** list in the Mixture Properties section, enter the names of the dependent variables in the **Molar concentration** column. When **Concentrated species** is selected, enter the names of the dependent variables in the **Mass fraction** column.

Surface Species

Specify the concentration of surface species in the table in this section.

The species present in this section will not be used to define mixture properties.

Solid Species

Specify the concentration of solid species in the table in this section.

The species present in this section will not be used to define mixture properties.

Aqueous Species

Specify the concentration of solid species in the table in this section.

The species present in this section will not be used to define mixture properties.

Thermodynamics Coupling

When coupled to Thermodynamics is enabled, the species in the Chemistry interface can be matched to the species in the Thermodynamic System. This is needed to ensure that arguments for the thermodynamic functions are correctly defined. Use the drop-down lists in the **From Thermodynamics** column to match each species in the interface to a species in the coupled thermodynamic system. For each species matched, the required property parameters and functions are added under the corresponding thermodynamic system. When all species are matched, the interface is considered fully coupled and functions representing mixture properties, such as the density, are also added automatically under the corresponding thermodynamic system.

Equilibrium Reaction Rate Table

This table is only available when equilibrium reactions are present in the interface. Use the **Reaction rate** column to specify the rate for each equilibrium reaction. By doing so the postprocessing variable for the total reaction rate for each species, of form

`chem.Rsum_species`, will be updated correctly. For a mass transport interface, say Transport of Diluted Species, the reaction rate needed for an equilibrium reaction is typically a dependent variable. In that case, the name of the variable can be found in the **Shape Function** section of the **Equation View** of the node.

When the Chemistry interface is created using from the **Generate Space-Dependent Model** the table is automatically set up in accordance with the added equilibrium reaction nodes.

CALCULATE TRANSPORT PROPERTIES

Select the **Calculate mixture properties** check box to calculate mixture properties that can be picked up in the space-dependent model interfaces. The properties that can be calculated are shown beneath the check box. Consider also if the built-in **Automatic** expressions fits the model or if **User defined** expressions are more suitable. In general, the Chemistry interface calculates properties in the same way as the Reaction Engineering interface.

Transport Properties

ACTIVITY

Select the **Use activity** check box to solve for species activities instead of species concentrations, which is a common approach when non-ideal fluids are modeled.

An activity coefficient other than 1 can be set for each species for the Species node in the **Species Concentration/Activity** section.

Activity

CHEMKIN IMPORT FOR SPECIES PROPERTIES

This section enables CHEMKIN® import to simulate complex chemical reactions in gas phase.

Two types of CHEMKIN input files can be imported here: **Thermo** and **Transport**, for thermodynamic properties and transport properties, respectively. Properties for either volumetric or surface species are supported. Click **Browse** to locate the CHEMKIN file to be imported, then click **Import**. For **Thermo**, the imported data is directly entered in

the **NASA format** fields in the Species node's **Thermodynamic Expressions** section; for **Transport**, the imported data is entered in its **Transport Expressions** section.

- CHEMKIN Data and NASA Polynomials
- Reversible Reaction Group

EXTRA DIMENSION

Select **Define variables in extra dimension** when the current Chemistry interface is coupled to a feature on an extra dimension. An example of this is when the concentrations in the **Concentration input** column of the **Model Inputs, Concentration** correspond to pellet concentrations from a Transport of Diluted Species interface's Reactive Pellet Bed feature.

When selected, generated variables will be defined using concentrations averaged over the extra dimension. Note that the generated variables are global in order be available on the main geometry, in contrast to variables on the extra dimension which only exist on the corresponding dimension.

Feature Nodes Available for the Chemistry Interface

The following feature nodes are available from the **Chemistry** ribbon toolbar (Windows users), **Chemistry** context menu (Mac or Linux users), or right-click to access the context menu (all users).

- Equilibrium Reaction Group
- Reaction
- Reaction Thermodynamics[1]
- Reversible Reaction Group
- Species
- Species Activity
- Species Group
- Species Thermodynamics[1]

[1] This is a subnode and it is only available together with a parent node.

Reaction

To add a **Reaction** node ( ) either right-click the **Chemistry** node or on the **Chemistry** toolbar click **Reaction**.

REACTION FORMULA

Formula

Enter a chemical reaction **Formula**. Click **Apply** to make the interface examine the species taking part in the model's reactions and automatically add the associated Species features to the Model Builder.

Balance ( )

If all species are written using their chemical formula, the stoichiometric coefficients can automatically be calculated, if the problem is well posed, by clicking the **Balance** button to the right of the **Reaction Formula** section title. This turns e.g. the formula "H2+O2=>H2O" into "2H2+O2=>2H2O".

Examples of problems that are not well posed are for example "C+H2=>CH4+C2H6", from which any ratio of CH_4/C_2H_6 could be obtained, and "H2=>O2", where not all elements are present on both sides.

Reaction Type

Select the **Reaction type** — **Reversible**, **Irreversible**, or **Equilibrium** — or edit the expression directly in the **Formula** field. In the latter case, specify the reaction type with a delimiter separating the two sides of the equation:

- <=> denotes a **Reversible** reaction
- => denotes an **Irreversible** reaction
- = denotes a reaction at chemical **Equilibrium**

Each **Reaction type** has its own set of reaction kinetics:

- If the reaction is **Reversible** or **Irreversible**, the reaction rate for reaction i contributes to the change in species i as follows:

$$R_i = \sum_i \nu_{ij} r_j \tag{2-98}$$

where ν_{ij} is the stoichiometric coefficient.

- If it is an **Equilibrium** reaction, the equilibrium expression is equal to the equilibrium constant:

$$K_{\text{eq}} = K_{\text{eq}0}$$

REACTION RATE

This section is available when the **Reaction type** is either **Reversible** or **Irreversible**.

When **Mass action law** is selected (default), the rate expression is automatically derived from the stoichiometric coefficients in the reaction formula:

- For an **Irreversible** reaction type, the reaction rate becomes:

$$r_j = k_j^{\mathrm{f}} \prod_{i \in \text{ react}} c_i^{-\nu_{ij}} \tag{2-99}$$

- For a **Reversible** reaction type, the expression instead becomes:

$$r_j = k_j^{\mathrm{f}} \prod_{i \in \text{ react}} c_i^{-\nu_{ij}} - k_j^{\mathrm{r}} \prod_{i \in \text{ prod}} c_i^{\nu_{ij}} \tag{2-100}$$

The deduced overall reaction order is shown in text below the respective equation in the **Reaction Rate** section.

Arbitrary Rate Expression

If the reaction order differs from the stoichiometric coefficients, or if an arbitrary rate expressions is applicable, change **Reaction Rate** to **User defined**. An expression field r appears with the default expression being that from the mass action law. Below this there are fields to set the reaction order. For a reversible reaction the reverse reaction order may be specified in addition to the forward one. The unit of the rate constant k (or frequency factor A in the case of Arrhenius behavior), is derived from the reaction order, in SI units: $(\mathrm{m}^3/\mathrm{mol})^{\alpha-1}/\mathrm{s}$, where α equals the order with respect to volumetric specfies. When surface species are present — identified by their "(ads)" suffix — the unit is instead given by $\mathrm{m}^{3\alpha+2\beta-2}/\mathrm{mol}^{\alpha+\beta-1}/\mathrm{s}$, where β is the order with respect to surface species.

Consider for example the reaction:

$$2\ S_2O_4^{2-} + H_2O \Rightarrow S_2O_3^{2-} + 2\ HSO_3^-$$

The automatically deduced reaction order is three, however, in the case that water is the solvent, the order should probably be two. This is specified as follows:

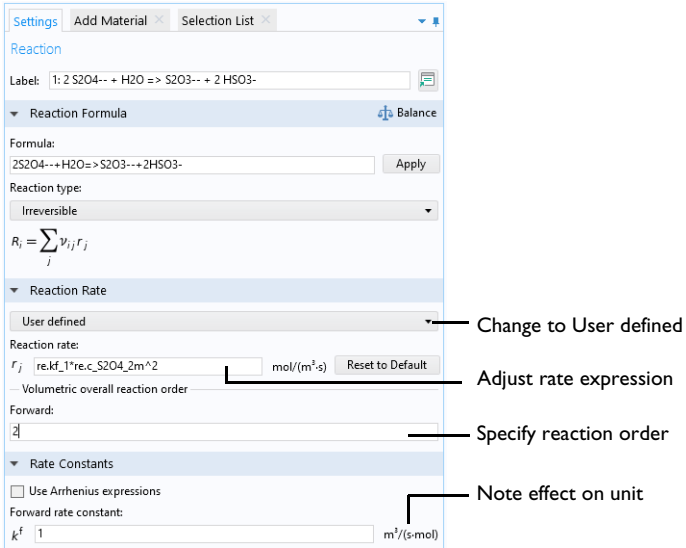


Figure 2-10: The reaction order can be manually specified for a user defined reaction rate.

RATE CONSTANTS

This section applies for **Reversible** or **Irreversible** reactions and defines the reaction rate constants used in the reaction rates.

Forward Rate Constant and Reverse Rate Constant

The **Forward rate constant** k^{f} is used for both **Reversible** and **Irreversible** reactions. The **Reverse rate constant** k^{r} is only used for **Reversible** reactions (Equation 2-99).

The SI units of the rate constants are automatically based on the order of the reaction with respect to the concentrations, as defined in the **Reaction formula**.

Specify Equilibrium Constant

The **Specify equilibrium constant** check box is available for **Reversible** reactions. If the check box is selected the rate constants are defined in a different manner with the reverse rate constant being computed from the following expression:

$$k^{\mathrm{r}} = k^{\mathrm{f}}/K_{\mathrm{eq}0}$$

Thus, in this case, the forward rate constant and equilibrium constant for the reaction are needed. The **Equilibrium constant** is edited in the Equilibrium Settings section.

Use Arrhenius Expressions

When the **Use Arrhenius expressions** check box is selected the Arrhenius parameters are automatically used in predefined expressions for the forward and reverse rate constants k^{f} and k^{r}, respectively.

$$k^{\mathrm{f}} = A^{\mathrm{f}}(T/T_{\mathrm{ref}})^{n^{\mathrm{f}}}\exp(-E^{\mathrm{f}}/(R_{\mathrm{g}}T))$$

$$k^{r} = A^{r}(T/T_{\mathrm{ref}})^{n^{\mathrm{r}}}\exp(-E^{\mathrm{r}}/(R_{\mathrm{g}}T))$$

Specify the activation energy and the frequency factor in the Arrhenius expressions to account for temperature variations. The reference temperature, T_{ref} equals 1 K. The available fields are based on the **Reaction type** chosen in the Reaction node. Enter values or expressions for each of the following (reverse expressions are only available for reversible reactions):

- **Forward frequency factor** A^{f} and **Reverse frequency factor** A^{r} (unit depends on reaction order)
- **Forward temperature exponent** n^{f} and **Reverse temperature exponent** n^{r}
- **Forward activation energy** E^{f} and **Reverse activation energy** E^{r} (SI unit: J/mol)

EQUILIBRIUM SETTINGS

This section is available for equilibrium reactions, and for reversible reactions when the **Specify equilibrium constant** check box has been selected.

Equilibrium Expression

For an equilibrium reaction, specify the **Equilibrium expression**. When the **Equilibrium expression** is set to **Automatic** the following expression is used:

$$K_{\mathrm{eq},j} = \frac{\prod_{i \in \mathrm{prod}} c_i^{\nu_{ij}}}{\prod_{i \in \mathrm{react}} c_i^{-\nu_{ij}}}$$

Select **User defined** from the **Equilibrium expression** list to instead enter a manually defined equilibrium expression.

Equilibrium Constant

Specify the **Equilibrium constant** K_{eq0} for an equilibrium reaction, or for a reversible reaction when the **Specify equilibrium constant** check box has been selected (in the **Rate Constants** section).

The **Equilibrium constant** can either be **User defined**, or automatically defined when set to **Automatic** or **Thermodynamics**.

Use the **Automatic** option to compute the equilibrium constant for an ideal system.

The **Thermodynamics** option is available when all reactions in the interface are equilibrium reactions, and the interface is fully coupled to a Thermodynamic System (see Species Matching). Use this setting to automatically compute the equilibrium constant for an ideal or nonideal system, dependent on the thermodynamic model applied for the coupled system.

Using **Automatic** or **Thermodynamics**, K_{eq0} is calculated from the Gibbs free energy of the reaction. For more details see The Equilibrium Constant and the Automatically Defined Equilibrium Constants section therein.

REACTION THERMODYNAMIC PROPERTIES

This section contains information about thermodynamic properties that relate to a selected reaction. Several **Automatic** definitions are available here.

Enthalpy of Reaction

The **Enthalpy of reaction** H (SI unit: J/mol) is calculated by the interface from species properties and the related stoichiometric coefficients:

$$H_j = \sum_{i \in \text{prod}} \nu_{ij} h_i - \sum_{i \in \text{react}} (-\nu_{ij}) h_i \tag{2-101}$$

Entropy of Reaction

The **Entropy of reaction** S (SI unit: J/(mol·K)) comes from a similar expression:

$$S_j = \sum_{i \in \text{prod}} \nu_{ij} s_i - \sum_{i \in \text{react}} (-\nu_{ij}) s_i \tag{2-102}$$

In Equation 2-101 and Equation 2-102, h_i and s_i are the species' molar enthalpy and molar entropy, respectively.

Enter these quantities in the **Species Thermodynamic Expressions** section for the Species node either by using the predefined polynomial or by providing a custom expression or constants.

The stoichiometric coefficients, ν_{ij}, are defined as being negative for reactants and positive for products. Using Equation 2-101 and Equation 2-102 to equate the Gibbs free energy of reaction enables the equilibrium constant to be expressed according to Equation 2-101.

Heat Source of Reaction

The **Heat source of reaction** (SI unit: W/m^3) is automatically computed from the heat of each reaction j, given by:

$$Q_j = -H_j r_j$$

Using the Reaction Node

Species

When a Reaction is defined, a **Species** node ( ) is automatically generated for the participating reactants and products. This feature enables you to review and enter species specific information regarding chemical kinetics, thermodynamics and transport properties.

It is also possible to add and define an individual **Species** node: on the **Chemistry** toolbar click **Species** or right-click the **Chemistry** node and select it from the context menu.

SPECIES NAME

When a **Species** node is automatically generated using the **Formula** text field for the Reaction node, the **Species name** is also automatically generated.

For a **Species** node added individually, enter a **Species name** in the field and click **Apply**.

Creating Valid Species Names and Labeling

SPECIES TYPE

Select a species type — **Bulk species**, **Surface species**, or **Solvent**.

Bulk species and **Solvent** are solved for volumetric concentrations (SI unit: mol/m^3), while **Surface species** are solved for surface concentration (SI unit: mol/m^2). The compositions for **Bulk species** and **Solvent** use the syntax `c_speciesname`, while **Surface species** uses `csurf_speciesname_surf`.

When **Surface species** is selected, the corresponding reaction formula introduces **(ads)** after the species notation and changes the species' name to `speciesname_surf`. Additionally, the Species node name is updated in a similar fashion.

GENERAL PARAMETERS

The **General Parameters** section deals with species parameters.

The default value for the **Molar mass**, M, and the ionic **Charge**, z, of the species is automatically defined from the species name by assuming that it corresponds to its chemical formula. Provided that the formula contains elements from the periodic table, the species molar mass is computed from mass the of occurring individual elements[2]. When the species name contains parts not in the periodic table, for example when a descriptive name such as `water` is used, the molar mass is set to 0.0 kg/mol and the charge to zero. In this case, the molar mass needs to be defined in order to achieve mass balanced reactions and correct definitions of mass basis properties. The species charge is also deduced from the species name. Creating a `H+` species, the charge will be set to one. When needed, both the **Molar mass** and the **Charge** can be edited in the corresponding edit field.

It is possible to specify the species density ρ when the fluid **Mixture** is specified as **Liquid**. The default value is that of water at 293 K.

REACTION RATE

Change the **Automatic** default setting to **User defined** to use a species reaction rate other than the one set up in the associated Reaction node. For individual species, use the **User defined** option to set a reaction rate other than zero (that is, nonreactive).

Edit either the **Rate expression** (SI unit: mol/(m^3·s)), the **Surface rate expression** (SI unit: mol/(m^2·s)), or both. For a bulk species, both expressions appear if surface reactions are present in the reactor since the reaction of the species can depend both on bulk reaction R and surface reaction R_{ads} rates. For a surface species, only the surface reaction rate R_{ads} appears.

2. Values are averages of upper and lower bounds for each atom as published by CIAAW. Source: CIAAW. Atomic weights of the elements 2019. Available online at www.ciaaw.org.

ADDITIONAL SOURCE

The **Additional Source** section is available in order to include additional rate contribution for the species to the reaction kinetics. When the **Additional source** check box is selected, add an **Additional rate expression** in the text field (SI unit: $\mathrm{mol/m^3}$).

SPECIES CONCENTRATION/ACTIVITY

To account for non-ideality in the fluid mixture, adjust the activity coefficient in the **Activity coefficient** input field. This input field is only shown if activity instead of concentration has been chosen in the interface, that is, the **Use activities** check box is selected on the Chemistry interface **Settings** window

Click to select the **Constant concentration/activity** check box if the species concentration or activity should be treated as constant.

SPECIES TRANSPORT EXPRESSIONS

Here the required parameters to compute various transport properties can be edited. To show this section the **Calculate mixture properties** check box needs to be selected under the **Calculate Transport Properties** section.

- For a gas mixture, there are maximum five properties to consider: σ, the characteristic length (unit: Å) of the Lennard-Jones/Stockmayer potential; ε/k_b, the energy minimum (SI unit: K) of the Lennard-Jones/Stockmayer potential; μ_D, the dipole moment (SI unit: Debye); k_i, the thermal conductivity of the gas (SI unit: W/(m K)); and Diffusivity of the species (SI unit: $\mathrm{m^2/s}$). The latter two can be set as **Automatic**, when theoretical Transport Parameters expressions are available.
- For mixtures of gas with solvent, all properties above except the thermal conductivity is shown. This is instead calculated under the **Calculate mixture properties** section on the Settings window for the Chemistry interface. This requires that the Feature Nodes Available for the Chemistry Interface check box is selected on the Chemistry interface **Settings** window.
- For a liquid mixture, there is only the parameter k_i, the thermal conductivity (SI unit: W/(m K)) to edit.
- For mixtures of liquid with solvent, the thermal conductivity is shown only for the species set as **Solvent**.

SPECIES THERMODYNAMIC EXPRESSIONS

The parameters utilized for calculation of thermodynamic mixture and reaction properties are set in this section.

The **Species Thermodynamic Expressions** are by default computed using data input in the **NASA format**. In this case, enter the following to compute the species' heat capacity, C_p (SI unit: J/(mol·K)), the molar enthalpy, h (SI unit: J/mol), and the molar entropy, s (SI unit: J/(mol·K)):

- **Lower temperature limit** T_{lo}
- **Middle temperature limit** T_{mid}
- **Upper temperature limit** T_{hi}
- **Polynomial coefficients** $a_{low,k}$ and $a_{hi,k}$

Any coefficients for the thermodynamic polynomials entered into the $a_{low,k}$ fields apply to the temperatures in the range T_{lo} to T_{mid}; coefficients entered into the $a_{hi,k}$ fields apply to temperatures in the range T_{mid} to T_{hi} range. The coefficients can also be imported in the **CHEMKIN Import for Species Properties** section in the Chemistry node.

Choose the **User defined** alternative to specify C_p, h, and s directly.

Using the Species Node

Reversible Reaction Group

The **Reversible Reaction Group** node ( ) allows input of a large number of reversible reactions in the same table. All reactions are treated in the same way. More than one Reversible Reaction Group can be added to a component. The feature is typically used when importing CHEMKIN kinetics files.

Add the node from the **Chemistry** toolbar or right-click **Chemistry** and add it from the context menu.

For the case when reaction kinetics data are entered manually into the **Reaction table** and temperature dependent reaction kinetics apply (Feature Nodes Available for the Chemistry Interface check box is selected), right-click to add a Reaction Thermodynamics subnode or select it from the **Chemistry** toolbar, **Attributes** menu. In it, the Enthalpy of Reaction (J/mol) for each reaction can be specified.

REACTION TABLE

The reversible reactions in the **Reaction table** are numbered and contain reactants, products, and kinetic parameters describing the reaction. Use the buttons under the **Reaction table** to add and sort the reaction details.

- In general, use the **Move Up** ( ), **Move Down** ( ), and **Delete** ( ) buttons and the fields under tables to edit the table contents. Or right-click a table cell and select **Move Up**, **Move Down**, or **Delete**.
- The **Add** button ( ) adds default reactant, A, and product, B, with a default. Click the corresponding field to edit the reactant, product, or parameters. After editing the Species Group node is also updated. It is created together with the reaction group.
- You can save the parameters to a text file to reuse in other models. Click the **Save to File** button ( ) and enter a **File name** in the **Save to File** dialog box, including the extension `.txt`. Click **Save** to store the parameters in a text file or in a Microsoft Excel Workbook spreadsheet if the license includes LiveLink™ *for* Excel®. The information is saved in space-separated columns in the same order as displayed on screen. When saving to Excel, an **Excel Save** dialog box appears where you can specify the sheet and range and whether to overwrite existing data or include a header.
- You can import or load data in files from a spreadsheet program, for example, with the **Load from File** button ( ) and the **Load from File** dialog box that appears. Data must be separated by spaces or tabs. If there is already data in the table, imported parameters are added after the last row. Move or edit rows as needed. If the license includes LiveLink™ *for* Excel® you can also load parameters from a Microsoft Excel Workbook spreadsheet. Then an **Excel Load** dialog box appears where you can specify the sheet and range and whether to overwrite existing data. It is also possible to import from a spreadsheet containing a separate column for units.

In the case of twenty or more reactions the **Disable updating variables during editing table** check box is available. Select this to speed up editing text fields; automatic updates related to edits do not occur until you click to clear the check box.

CREATE REACTION AND SPECIES

Enter a reaction number in the **Moving reaction (with the number) from table** text field and click **Create Reaction** to remove the reaction from the **Reaction table** to the model tree. This introduces a reaction node named after the reaction number and species names and simultaneously creates corresponding species nodes. This action is powerful, since it enables all the editing possibilities available for Reaction and Species nodes.

CHEMKIN IMPORT FOR KINETICS

Click to select the **Import CHEMKIN data** check box to import a CHEMKIN **Kinetics input file**. To import the data directly into the table columns, click **Browse** to locate the CHEMKIN file to be imported, then click **Import**.

CHEMKIN Data and NASA Polynomials

Equilibrium Reaction Group

The **Equilibrium Reaction Group** node ( ) allows for input of a large number of equilibrium reactions in the same table. This node functions in the same way as the Reversible Reaction Group for reversible reactions.

Add the node from the **Chemistry** toolbar or right-click **Chemistry** and add it from the context menu.

For the case when reaction kinetics data are entered manually into the **Reaction table** and temperature dependent reaction kinetics apply (Feature Nodes Available for the Chemistry Interface check box is selected), right-click to add a Reaction Thermodynamics subnode or select it from the **Chemistry** toolbar, **Attributes** menu. In it, the Enthalpy of Reaction (J/mol) for each reaction can be specified.

REACTION TABLE

The equilibrium reactions in the **Reaction table** are numbered and contain reactants, products, and kinetic parameters describing the reaction. Use the buttons under the **Reaction table** to add and sort the reaction details.

- In general, use the **Move Up** ( ), **Move Down** ( ), and **Delete** ( ) buttons and the fields under tables to edit the table contents. Or right-click a table cell and select **Move Up**, **Move Down**, or **Delete**.
- The **Add** button ( ) adds default reactant, A, and product, B, with a default. Click the corresponding field to edit the reactant, product, or parameters. After editing the Species Group node is also updated. It is created together with the reaction group.
- You can save the parameters to a text file to reuse in other models. Click the **Save to File** button ( ) and enter a **File name** in the **Save to File** dialog box, including the extension `.txt`. Click **Save** to store the parameters in a text file or in a Microsoft Excel Workbook spreadsheet if the license includes LiveLink™ *for* Excel®. The

information is saved in space-separated columns in the same order as displayed on screen. When saving to Excel, an **Excel Save** dialog box appears where you can specify the sheet and range and whether to overwrite existing data or include a header.

- You can import or load data in files from a spreadsheet program, for example, with the **Load from File** button ( ) and the **Load from File** dialog box that appears. Data must be separated by spaces or tabs. If there is already data in the table, imported parameters are added after the last row. Move or edit rows as needed. If the license includes LiveLink™ *for* Excel® you can also load parameters from a Microsoft Excel Workbook spreadsheet. Then an **Excel Load** dialog box appears where you can specify the sheet and range and whether to overwrite existing data. It is also possible to import from a spreadsheet containing a separate column for units.

In the case of twenty or more reactions the **Disable updating variables during editing table** check box is available. Select this to speed up editing text fields; automatic updates related to edits do not occur until you click to clear the check box.

	Chemical Vapor Deposition of GaAs: Application Library path **Chemical_Reaction_Engineering_Module/Reactors_with_Mass_and_Heat_Transfer/gaas_cvd**

Species Group

The **Species Group** node ( ) contains information on a molecular level about the volumetric species and the surface species present in the model. The **Property for Volumetric Species** or **Property for Surface Species** tables typically collect parameters from when importing CHEMKIN transport files.

This node is also automatically added when either the Reversible Reaction Group or the Equilibrium Reaction Group are used.

For the case of temperature dependent reaction kinetics (Feature Nodes Available for the Chemistry Interface check box is selected), a Species Thermodynamics subnode is automatically created in which the thermodynamic properties of the species can be specified.

CHEMKIN

This section allows import of CHEMKIN transport files. To import the data directly into the table columns, click **Browse** to locate the CHEMKIN file to be imported, then click **Import**. Note that this section is only shown when transport properties are

computed (**Calculate mixture properties** check box under the **Calculate Transport Properties** is selected).

CHEMKIN Data and NASA Polynomials

Reaction Thermodynamics

The **Reaction Thermodynamics** subnode ( ), the Enthalpy of Reaction (J/mol) of each reaction can be specified. This node overrides all the automatically calculated reaction enthalpies as defined in the Species Thermodynamics subnode.

Add the **Reaction Thermodynamics** node from the **Chemistry** toolbar, **Attributes** menu. Alternatively, when the Feature Nodes Available for the Chemistry Interface check box is selected on the Chemistry interface **Settings** window, right-click a Reversible Reaction Group or Equilibrium Reaction Group to add the **Reaction Thermodynamics** subnode.

Species Activity

The **Species Activity** node (ai) creates variables for the activities of all the species/surface species present in the Species Group parent feature. Edit the **Activity coefficient** field in the **Species Activity** or **Surface Species Activity** tables by clicking in these.

Species Activity is a subnode to the Species Group node. It is automatically generated when nonideality in the fluid mixture is accounted for; when the **Use activity** check box is selected in the **Activity** section.

Species Thermodynamics

The **Species Thermodynamics** node ( ) creates variables for the enthalpies, entropies, and heat capacities for all the species/surface species present in the Species Group parent feature. The purpose is to compute thermodynamic mixture properties and the heat of reactions.

This node is a subnode to the Species Group node when the Feature Nodes Available for the Chemistry Interface check box is selected on the Chemistry interface **Settings** window.

SPECIES THERMODYNAMICS PROPERTY

Select a **Type selection** for the thermodynamic properties. The **NASA format** alternative requires the setting of several polynomial constants and is typically used together with CHEMKIN import. The **User defined** alternative only requires input of Species molar enthalpy (J/mol) and Species molar capacity (J/(mol·K)).

CHEMKIN IMPORT FOR THERMODYNAMIC DATA

This section allows import of thermodynamic CHEMKIN transport files. To import the data directly into the table columns, click **Browse** to locate the CHEMKIN file to be imported, then click **Import**. Note that this can only be done for the **NASA format** option.

- CHEMKIN Data and NASA Polynomials

Study Steps for the Reaction Engineering Interface

Reactor Types and Solver Study Steps

The predefined **CSTR**, **Batch** and **Semibatch** reactor types available in the Reaction Engineering interface set up equations describing how species concentrations in a perfectly mixed system change with time. **Time Dependent** is the correct study type to use for these reactor types. The simulation time is specified in the settings of the **Time Dependent** study step.

The predefined **Plug flow** reactor type sets up equations for stationary conditions describing how species molar flow rates (SI unit: mol/s) vary with the reactor volume. **Stationary Plug Flow** is the correct study type to use for this reactor type. The reactor volume is specified in the **Stationary Plug Flow** study step feature

Note that selecting the **Reaction Engineering** interface and the **Time Dependent** study sets up the **Batch, constant volume** reactor type by default. The **Time Dependent** study is also suitable for all **CSTR** reactors and the **Semibatch** reactor. However, if the reactor type is changed to **Plug flow**, then the Time Dependent study step needs to be replaced with a **Stationary Plug Flow** step. Combining a Reaction Engineering interface with the **Stationary Plug Flow** study does not set up a **Plug flow** reactor type by default. In that situation, the **Plug Flow** reactor type needs to be set manually in the Reaction Engineering interface.

Solver Study Steps for Parameter Estimation

Parameter Estimation calculations are enabled in the **Study** branch, by right-clicking the study node and selecting the **Optimization** study step from the context menu. Moving to the main **Study** node and clicking **Compute** starts the parameter estimation.

The **Optimization Solver** node is a subnode to the **Solver** node. In the settings window the **Optimization Solver** section offers the several methods for solving the optimization problem.

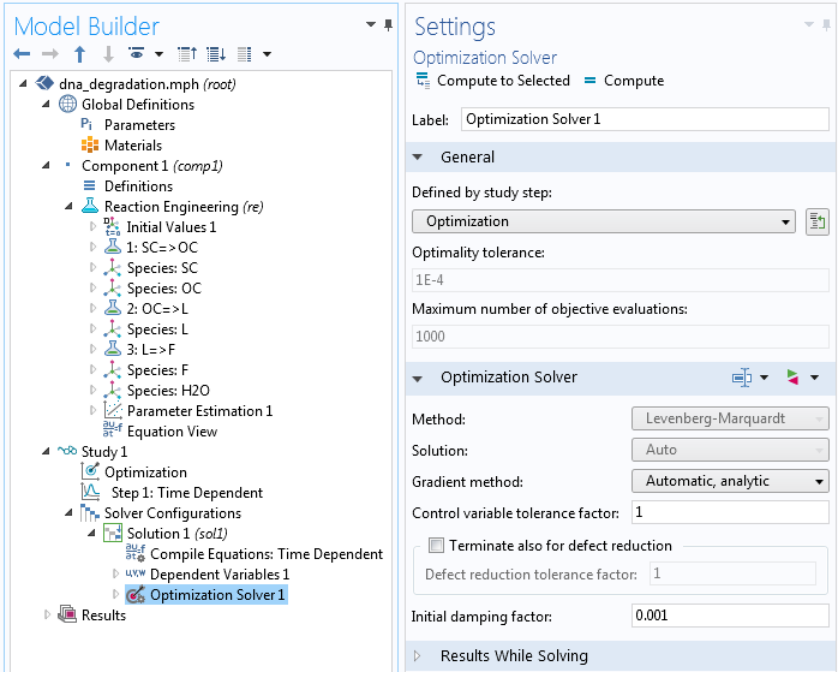


Figure 2-11: The settings for the Optimization Solver are accessed in the Study tree.

www.comsol.com/optimization-module

3

Chemical Species Transport Interfaces

The **Chemical Species Transport** branch ( ) includes a number of subbranches to describe mass transport and chemical reactions. The physics interfaces are summarized in the first section, and then described in detail throughout this chapter. All physics interfaces include features for defining arbitrary reaction kinetics, to be used as mass sources and sinks, as well as arbitrary mass transport parameters.

- Overview of Chemical Species Transport Interfaces
- Theory for the Transport of Diluted Species Interface and the other transport interfaces.
- The Transport of Diluted Species Interface
- The Transport of Diluted Species in Porous Media Interface
- The Transport of Diluted Species in Fractures Interface
- The Transport of Concentrated Species Interface
- The Nernst–Planck Equations Interface
- The Nernst–Planck-Poisson Equations Interface
- The Electrophoretic Transport Interface
- The Surface Reactions Interface

- The Reacting Flow Multiphysics Interface
- The Reacting Flow in Porous Media Multiphysics Interface

Note that The Chemistry and Reaction Engineering Interfaces and The Chemistry Interface are described in The Chemistry and Reaction Engineering Interfaces chapter.

Overview of Chemical Species Transport Interfaces

In this section:

- Available Physics Interfaces
- Coupling to Other Physics Interfaces
- Adding a Chemical Species Transport Interface and Specifying the Number of Species

Available Physics Interfaces

THE SURFACE REACTIONS (SR) INTERFACE

The Surface Reactions Interface ( ) models reactions involving surface adsorbed species and species in the bulk of a reacting surface. The physics interface is typically active on a model boundary and is coupled to a mass transport physics interface active on a model domain. The Surface Reactions interface can be used together with other Chemical Species Transport interfaces, the Reacting Flow interfaces, and the Electrochemistry interfaces. Predefined expressions for the growth velocity of the reacting surface makes it easy to set up models with moving boundaries. Also see the Theory for the Surface Reactions Interface.

The Electrochemistry interfaces require the addition of the Battery Design Module, the Corrosion Module, the Electrochemistry Module, the Electrodeposition Module, or the Fuel Cell & Electrolyzer Module.

THE TRANSPORT OF DILUTED SPECIES AND TRANSPORT OF DILUTED SPECIES IN POROUS MEDIA (TDS) INTERFACES

The mass transfer equations account for chemical species transport by diffusion, convection, and migration due to an electric field (electrokinetic flow)—either alone or in combination. The Transport of Diluted Species Interface ( ) is an enhanced version of the physics interface included with the basic COMSOL Multiphysics license and is applicable for solutions (either fluid or solid) where the transported species have concentrations at least one order of magnitude less than the solvent. The settings for this physics interface can be chosen so as to simulate chemical species transport

through diffusion (Fick's law), convection (when coupled to fluid flow), and migration (when coupled to an electric field — electrokinetic flow).

The Transport of Diluted Species in Porous Media Interface ( ) is tailored for the modeling of solute transport in porous media. The physics interface supports cases where either the solid phase substrate is exclusively immobile, or when a gas-filling medium is also assumed to be immobile.

THE TRANSPORT OF CONCENTRATED SPECIES (TCS) INTERFACE

The Transport of Concentrated Species Interface ( ) is used for modeling transport within mixtures where no one component is clearly dominant. Often the concentrations of the participating species are of the same order of magnitude, and the molecular effects of respective species on each other needs to be considered. This physics interface supports transport through Fickian diffusion, a mixture-average diffusion model, and as described by the Maxwell-Stefan equations. These take into account the diffusion properties of all species with respect to each other. Convective transport and transport by migration in electric fields are also accounted for by this physics interface. Also see the Theory for the Transport of Diluted Species Interface.

THE NERNST–PLANCK EQUATIONS (NPE) INTERFACE

The Nernst–Planck Equations Interface ( ) includes a migration term, along with convection and diffusion mass transport, together with an equation that guarantees electroneutrality. A term to describe the electric potential is also provided in the physics interface itself. Also see the Theory for the Nernst–Planck Equations Interface.

THE REACTING FLOW IN POROUS MEDIA (RFP) INTERFACES

The Reacting Flow in Porous Media, Transport of Diluted Species Interface ( ) (found under the **Chemical Species Transport>Reacting Flow in Porous Media** branch ( ) when adding a physics interface), is a multiphysics interface treating diluted reacting mixtures transported by a porous media flow. The nonlocal coupling for the velocity field is set up automatically.

The Reacting Flow in Porous Media, Transport of Concentrated Species Interface( ) found under the **Chemical Species Transport>Reacting Flow in Porous Media** branch ( ) when adding a physics interface), is a multiphysics interface treating concentrated reacting mixtures transported by a porous media flow. The couplings between velocity field and mixture density are set up automatically.

The next sections, Coupling to Other Physics Interfaces and Adding a Chemical Species Transport Interface and Specifying the Number of Species provide more information to help you start modeling.

Coupling to Other Physics Interfaces

When using this module you are often simulating applications that can be described by the mass transport interfaces in the Chemical Species Transport branch. Yet, as a lot of mass transport is dependent on convection, couplings to Fluid Flow interfaces are required. COMSOL Multiphysics and the Chemical Reaction Engineering Module include physics interfaces for laminar flow as well as porous media flow. More advanced descriptions of fluid flow, such as turbulent flow and multiphase flow, require the CFD Module.

Most chemical reactions or other type of material processing, such as casting, either require or produce heat, which in turn affects both the reaction and other physical processes connected to the system. Heat transfer through conduction and convection, when flow is laminar, as well as through porous media are supported in this module. More extensive description of heat transfer, such as in turbulent flow or involving radiation, require the Heat Transfer Module. The Heat Transfer Module also includes turbulent flow.

COMSOL Multiphysics easily supports simulations of electrostatics or DC-based physical phenomena, even if conductivity is nonlinear. If the electric field is AC/DC in nature, or if the system is affected by electromagnetic waves, then the AC/DC Module and RF Module have appropriate physics interfaces for these phenomena. Some applications of electrochemical reactions, particularly in electrochemical power source applications, are better handled by the Battery Design Module.

Adding a Chemical Species Transport Interface and Specifying the Number of Species

A chemical species transport interface can be added when first creating a new model, or at any time during the modeling process.

Creating a New Model in the *COMSOL Multiphysics Reference Manual*

1 To add a physics interface:

- Select **New** to open the **Model Wizard**, after selecting a space dimension, go to the **Select Physics** page.
- From the **Home** toolbar click **Add Physics** ( ). Or right-click the **Component** node in the **Model Builder** and select **Add Physics**. Go to the **Add Physics** window.

2 Under **Chemical Species Transport**, navigate to the physics interface to add and double-click it.

There are other ways to add a physics interface depending on whether you are in the Model Builder or Add Physics window:

- In the **Model Wizard**, click **Add** or right-click and select **Add Physics** ( ). The physics interface displays under **Added physics interfaces**.
- In the **Add Physics** window, click **Add to Component** ( ) or right-click and select **Add to Component**.

3 Specify the number of species (concentrations or mass fractions) and the names:

- In the **Model Wizard**, on the **Review Physics Interface** page under **Dependent Variables**.
- In the **Add Physics** window, click to expand the **Dependent Variables** section.
- After adding the physics interface, you can also edit this information—click the node in the **Model Builder**, then, on the **Settings** window under **Dependent Variables**, specify the information.

4 Continue by adding more physics interfaces and specifying the number of species (concentrations or mass fractions) that are to be simulated in a mass transport interface when adding that interface.

5 In the **Dependent Variables** section, enter the **Number of species**. To add a single species, click the **Add Concentration** button ( ) underneath the table or enter a value into the **Number of species** field. Click the **Remove Concentration** button ( ) underneath the table if required.

6 The **Transport of Concentrated Species** interface and the **Nernst–Planck Equations** interface both need to contain at least two species (the default). Also edit the strings or names directly in the table. The names must be unique for all species (and all other dependent variables) in the model.

7 For the **Nernst–Planck Equations** interface, an electric potential variable is also required.

The **Reaction Engineering** interface can automatically set up the reacting species and their dependent variables. If you plan on using chemistry from the Reaction Engineering interface in species transport interface, the *Generate Space Dependent Model* feature is recommended to set up the transport interface.

Theory for the Transport of Diluted Species Interface

The Transport of Diluted Species Interface provides a predefined modeling environment for studying the evolution of chemical species transported by diffusion and convection as well as migration due to an electric field. The physics interface assumes that all species present are dilute; that is, that their concentration is small compared to a solvent fluid or solid. As a rule of thumb, a mixture containing several species can be considered dilute when the concentration of the solvent is more than 90 mol%. Due to the dilution, mixture properties such as density and viscosity can be assumed to correspond to those of the solvent.

When studying mixtures that are not dilute, the mixture and transport properties depend on the composition, and a different physics interface is recommended. See The Transport of Concentrated Species Interface in the for more information.

Fick's law governs the diffusion of the solutes, dilute mixtures, or solutions, while the phenomenon of ionic migration is sometimes referred to as *electrokinetic flow*. The Transport of Diluted Species interface supports the simulations of chemical species transport by convection, migration, and diffusion in 1D, 2D, and 3D as well as for axisymmetric components in 1D and 2D.

In this section:

- Adding Transport Through Migration
- Convective Term Formulation
- Crosswind Diffusion
- Danckwerts Inflow Boundary Condition
- Equilibrium Reaction Theory
- Mass Balance Equation
- Mass Sources for Species Transport
- Solving a Diffusion Equation Only
- Supporting Electrolytes
- Theory for the Reactive Pellet Bed
- References

Note: Some features explained in this section require certain add-on modules. For details see https://www.comsol.com/products/specifications/

The section also includes the theory for The Transport of Diluted Species in Porous Media Interface:

- Adsorption
- Convection in Porous Media
- Diffusion in Porous Media
- Dispersion
- Mass Balance Equation for Transport of Diluted Species in Porous Media
- Mass Transport in Fractures
- Reactions

Mass Balance Equation

The default node attributed to the Transport of Diluted Species interface models chemical species transport through diffusion and convection and solves the mass conservation equation for one or more chemical species i:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{J}_i + \mathbf{u} \cdot \nabla c_i = R_i \tag{3-1}$$

Equation 3-1 in its form above includes the transport mechanisms diffusion and convection. If *Migration in Electric Field* is activated (only available in some add-on products), the migration mechanism will be added to the equation as well. See more details in the section Adding Transport Through Migration.

- c_i is the concentration of the species (SI unit: mol/m^3)
- D_i denotes the diffusion coefficient (SI unit: m^2/s)
- R_i is a reaction rate expression for the species (SI unit: mol/(m^3·s))
- $\mathbf{u}$ is the mass averaged velocity vector (SI unit: m/s)
- $\mathbf{J}_i$ is the mass flux diffusive flux vector (SI unit: mol/(m^2·s))

The mass flux relative to the mass averaged velocity, $\mathbf{J}_i$ (SI unit: mol/(m^2·s)), is associated with the mass balance equation above and used in boundary conditions and flux computations. The Transport of Diluted Species interface always includes mass transport due to molecular diffusion. In this case the mass flux $\mathbf{J}_i$ defines the diffusive flux vector

$$\mathbf{J}_i = -D\nabla c \tag{3-2}$$

An input field for the diffusion coefficient is available.

When *Migration in Electric Fields* is activated, the migration term is also added to the diffusive flux vector as shown in the section Adding Transport Through Migration.

The third term on the left side of Equation 3-1 describes the convective transport due to a velocity field **u**. This field can be expressed analytically or obtained from coupling the physics interface to one that solves for fluid flow, such as *Laminar Flow*. Note that all fluid flow interfaces solve for the mass averaged velocity.

On the right-hand side of the mass balance equation (Equation 3-1), R_i represents a source or sink term, typically due to a chemical reaction or desorption on a porous matrix. To specify R_i, another node must be added to the Transport of Diluted Species interface — the **Reaction** node for example, which includes an input field for specifying a reaction expression using the variable names of all participating species.

Equilibrium Reaction Theory

The feature Equilibrium Reaction is described in this section. A chemical equilibrium reaction system is defined by the stoichiometry of the reaction and the relation between the chemical activities of the chemical species participating in the reaction (the equilibrium condition).

The kinetics of the reaction is so fast that the equilibrium condition is fulfilled at all times in all space coordinates.

The equilibrium condition is commonly based on the stoichiometric coefficients, ν_i (dimensionless), of the reaction; the species activities of the reacting species a_i (dimensionless); and an equilibrium constant, K_{eq} (1) according to:

$$K_{\mathrm{eq}} = \frac{\prod_{i \in \text{ products}} a_i^{\nu_i}}{\prod_{i \in \text{ reactants}} a_i^{-\nu_i}}$$

where the species activities are defined as

$$a_i = \gamma_{c,i} \frac{c_i}{c_{\mathrm{a0}}}$$

where c_{a0} (SI unit: mol/m^3) is the standard molarity, and $\gamma_{c,i}$ (dimensionless) an activity coefficient.

Defining the stoichiometric coefficients positive for products and negative for reactants, the above equilibrium condition can also be written:

$$K_{\mathrm{eq}} = \prod_i a_i^{\nu_i}$$

The Equilibrium Reaction node solves for a reaction rate so that the equilibrium condition is always fulfilled in the domain. It is available for the Chemical Reaction Engineering Module; Battery Design Module; Corrosion Module; Electrochemistry Module; Electrodeposition Module; and Fuel Cell & Electrolyzer Module.

$\gamma_{c,i}$ is set to unity when the Equilibrium constant is selected on the Settings window. For nonunity activity coefficients, a user defined equilibrium condition can be used.

EQUILIBRIUM REACTIONS AND INFLOW BOUNDARY CONDITIONS

Contradictory constraints arise if the boundary conditions for concentrations or activities are set so that the domain equilibrium condition is not fulfilled. Special treatment is therefore needed at Inflow boundaries, where the concentrations are set for all species in the mass transport interfaces.

One way of avoiding competing constraints on an inflow boundary is to add an additional reaction coordinate degree of freedom, solved for to create a set of modified inflow concentrations that fulfill the domain equilibrium condition. The reaction coordinate gives rise to a concentration shift, which is the offset to the inflow concentrations provided by the user. The shift for each species obeys the stoichiometry of the reaction and the equilibrium expression. The modified inflow concentrations are then used in the boundary conditions for the domain mass transport equations. The resulting modified inflow concentrations can be seen as the stationary solution for a batch reactor with the user inflow concentrations as initial concentrations. In addition, the domain reaction rate degree of freedom of the equilibrium reaction is constrained to zero on all Inflow boundaries.

EQUILIBRIUM REACTIONS AND CONCENTRATION BOUNDARY CONDITIONS

No special treatment is made with regards to input concentration values of the Concentration boundary node. Using this feature, you can explicitly set one or a set of concentrations, and the equilibrium condition acts on the rest of the concentrations.

However, there is no solution to the problem if more concentrations than the number of species minus the number of equilibrium reactions are set using this feature.

EQUILIBRIUM REACTIONS AND TIME-DEPENDENT SIMULATIONS

Spurious oscillations may occur in a time-dependent problem if the initial conditions do not fulfill the equilibrium condition. Since equilibrium reactions are assumed to be infinitely fast, the solution is to initialize the problem using an additional study step, solving for a stationary problem with all nonequilibrium reaction rates set to zero. Manual scaling of the reaction rate dependent variables is needed in this study step.

Convective Term Formulation

The default node attributed to The Transport of Diluted Species Interface assumes chemical species transport through diffusion and convection (depending on the modules licensed, a check box to activate migration is available) and implements the mass balance equation in Equation 3-1.

There are two ways to present a mass balance where chemical species transport occurs through diffusion and convection. These are the nonconservative and conservative formulations of the convective term:

$$\text{nonconservative: } \frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c = \nabla \cdot \mathbf{J}_i + R \tag{3-3}$$

$$\text{conservative: } \frac{\partial c}{\partial t} + \nabla \cdot (c\mathbf{u}) = \nabla \cdot \mathbf{J}_i + R \tag{3-4}$$

and each is treated slightly differently by the solver algorithms. In these equations $\mathbf{J}_i$ (SI unit: mol/(m^2·s)) is the diffusive flux vector, R (SI unit: mol/(m^3·s)) is a production or consumption rate expression, and $\mathbf{u}$ (SI unit: m/s) is the solvent velocity field. The diffusion process can be anisotropic, in which case D is a tensor.

If the conservative formulation is expanded using the chain rule, then one of the terms from the convection part, $c\nabla\cdot\mathbf{u}$, would equal zero for an incompressible fluid and would result in the nonconservative formulation above. This is in fact the default formulation in this physics interface. To switch between the two formulations, click the **Show** button ( ) and select **Advanced Physics Options**.

Solving a Diffusion Equation Only

Remove the convection term from Equation 3-3 and Equation 3-4 by clearing the Convection check box in the Transport Mechanisms section for The Transport of Diluted Species Interface. The equation then becomes

$$\frac{\partial c}{\partial t} = \nabla \cdot \mathbf{J}_i + R$$

Mass Sources for Species Transport

Note: The features below are only available in a limited set of add-on products. For a detailed overview of which features are available in each product, visit https://www.comsol.com/products/specifications/

There are two types of mass sources in the Transport of Diluted Species interface: point sources and line sources.

POINT SOURCE

A point source is theoretically formed by assuming a mass injection/ejection, $\dot{Q}_c$ (SI unit: mol/(m^3·s)), in a small volume δV and then letting the size of the volume tend to zero while keeping the total mass flux constant. Given a point source strength, $\dot{q}_{p,c}$ (SI unit: mol/s), this can be expressed as

$$\lim_{\delta V \to 0} \int_{\delta V} \dot{Q}_c = \dot{q}_{p,c} \tag{3-5}$$

An alternative way to form a point source is to assume that mass is injected/extracted through the surface of a small object. Letting the object surface area tend to zero while keeping the mass flux constant results in the same point source. For this alternative approach, effects resulting from the physical object's volume need to be neglected.

The weak contribution

$$\dot{q}_{p,c}\text{test}(c)$$

is added at a point in the geometry. As can be seen from Equation 3-5, $\dot{Q}_c$ must tend to plus or minus infinity as δV tends to zero. This means that in theory the concentration also tends to plus or minus infinity.

Observe that "point" refers to the physical representation of the source. A point source can therefore only be added to points in 3D components and to points on the symmetry axis in 2D axisymmetry components. Other geometrical points in 2D components represent physical lines.

The finite element representation of Equation 3-5 corresponds to a finite concentration at a point with the effect of the point source spread out over a region around the point. The size of the region depends on the mesh and on the strength of the source. A finer mesh gives a smaller affected region but also a more extreme concentration value. It is important not to mesh too finely around a point source since this can result in unphysical concentration values. It can also have a negative effect on the condition number for the equation system.

LINE SOURCE

A line source can theoretically be formed by assuming a source of strength $\dot{Q}_{l,c}$ (SI unit: mol/(m^3·s)), located within a tube with cross section δS and then letting δS tend to zero while keeping the total mass flux per unit length constant. Given a line source strength, $\dot{q}_{l,c}$ (SI unit: mol/(m·s)), this can be expressed as

$$\lim_{\delta S \to 0} \int_{\delta S} \dot{Q}_{l,c} = \dot{q}_{l,c} \tag{3-6}$$

As in the point source case, an alternative approach is to assume that mass is injected/extracted through the surface of a small object. This results in the same mass source, but requires that effects resulting from the physical object's volume are neglected.

The weak contribution

$$\dot{q}_{l,c}\text{test}(c)$$

is added on lines in 3D or at points in 2D (which represent cut-through views of lines). Line sources can also be added on the axisymmetry line in 2D axisymmetry components. It cannot, however, be added on geometrical lines in 2D since those represent physical planes.

As with a point source, it is important not to mesh too finely around the line source.

For feature node information, see Line Mass Source and Point Mass Source.

For the Reacting Flow in Porous Media, Diluted Species interface, which is available with the CFD Module, Chemical Reaction Engineering Module, or Battery Design Module, these shared physics nodes are renamed as follows:

- The **Line Mass Source** node is available as two nodes, one for the fluid flow (**Fluid Line Source**) and one for the species (**Species Line Source**).
- The **Point Mass Source** node is available as two nodes, one for the fluid flow (**Fluid Point Source**) and one for the species (**Species Point Source**).

Adding Transport Through Migration

Note: Migration is only available in a limited set of add-on products. For a detailed overview of which features are available in each product, visit https://www.comsol.com/products/specifications/

In addition to transport due to convection and diffusion, the Transport of Diluted Species interface supports ionic species transport by *migration*. This is done by selecting the Migration in Electric Field check box under the Transport Mechanisms section for the physics interface. The mass balance then becomes:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i - z_i u_{\mathrm{m},i} F c_i \nabla V + c_i \mathbf{u}) = R_i \tag{3-7}$$

where

- c_i (SI unit: mol/ m^3) denotes the concentration of species i
- D_i (SI unit: m^2/s) is the diffusion coefficient of species i
- $\mathbf{u}$ (SI unit: m/s) is the fluid velocity
- F (SI unit: A·s/mol) refers to Faraday's constant
- V (SI unit: V) denotes the electric potential
- z_i (dimensionless) is the charge number of the ionic species, and
- $u_{\mathrm{m},i}$ (SI unit: mol·s/kg) is its ionic mobility

In this case the diffusive flux vector is

$$\mathbf{J}_i = -D_i \nabla c_i - z_i u_{\mathrm{m},i} F c_i \nabla V$$

The velocity, $\mathbf{u}$, can be a computed fluid velocity field from a Fluid Flow interface or a specified function of the spatial variables x, y, and z. The potential can be provided by an expression or by coupling the system of equations to a current balance, such as the Electrostatics interface. Sometimes it is assumed to be a supporting electrolyte present, which simplifies the transport equations. In that case, the modeled charged species concentration is very low compared to other ions dissolved in the solution. Thus, the species concentration does not influence the solution's conductivity and the net charge within the fluid.

The Nernst–Einstein relation can in many cases be used for relating the species mobility to the species diffusivity according to

$$u_{m,i} = \frac{D_i}{RT}$$

where R (SI unit: J/(mol·K)) is the molar gas constant and T (SI unit: K) is the temperature.

Note: In the *Nernst–Planck Equations* interface, the ionic species contribute to the charge transfer in the solution. It includes an *electroneutrality condition* and also computes the electric potential field in the electrolyte. For more information, see Theory for the Nernst–Planck Equations Interface. This interface is included in the Chemical Reaction Engineering Module.

Supporting Electrolytes

In *electrolyte* solutions, a salt can be added to provide a high electrolyte conductivity and decrease the ohmic losses in a cell. These solutions are often called *supporting electrolytes*, buffer solutions, or carrier electrolytes. The added species, a negative and a positive ion pair, predominates over all other species. Therefore, the supporting electrolyte species can be assumed to dominate the current transport in the solution. In addition, the predominant supporting ions are usually selected so that they do not react at the electrode surfaces since the high conductivity should be kept through the process, that is, they should not be electro-active species. This also means that the concentration gradients of the predominant species in a supporting electrolyte are usually negligible.

Modeling and solving for a supporting electrolyte in the *Electrostatics* or *Secondary Current Distribution* interfaces will give a potential distribution that drives the migration in the Transport of Diluted Species Interface.

The current density vector is proportional to the sum of all species fluxes as expressed by Faraday's law:

$$\mathbf{i} = F\sum_i z_i \mathbf{N}_i$$

The electroneutrality condition ensures that there is always a zero net charge at any position in a dilute solution. Intuitively, this means that it is impossible to create a current by manually pumping positive ions in one direction and negative ions in the other. Therefore, the convective term is canceled out to yield the following expression for the electrolyte current density, where j denotes the supporting species:

$$\mathbf{i} = F\sum_j -z_j^2 u_{\mathrm{m},j} F c_j \nabla\phi \tag{3-8}$$

Equation 3-8 is simply Ohm's law for ionic current transport and can be simplified to

$$\mathbf{i} = -\kappa\nabla\phi \tag{3-9}$$

where κ is the conductivity of the supporting electrolyte. A current balance gives the current and potential density in the cell

$$\nabla \cdot \mathbf{i} = 0$$

which, in combination with Equation 3-9, yields:

$$\nabla \cdot (-\kappa\nabla\phi) = 0 \tag{3-10}$$

Equation 3-10 can be easily solved using the Electrostatics or Secondary Current Distribution interface and, when coupled to the Transport in Diluted Species interface, the potential distribution shows up in the migration term.

Crosswind Diffusion

Transport of diluted species applications can often result in models with a very high cell Péclèt number — that is, systems where convection or migration dominates over diffusion. Streamline diffusion and crosswind diffusion are of paramount importance to obtain physically reasonable results. The Transport of Diluted Species interface

provides two crosswind diffusion options using different formulations. Observe that crosswind diffusion makes the equation system nonlinear even if the transport equation is linear.

DO CARMO AND GALEÃO

This is the formulation described in Numerical Stabilization in the *COMSOL Multiphysics Reference Manual*. The method reduces over- and undershoots to a minimum, even for anisotropic meshes.

In some cases, the resulting nonlinear equation system can be difficult to converge. This can happen when the cell Péclèt number is very high and the model contains many thin layers, such as contact discontinuities. You then have three options:

- Refine the mesh, especially in regions with thin layers.
- Use a nonlinear solver with a constant damping factor less than one.
- Switch to the Codina crosswind formulation.

CODINA

The Codina formulation is described in Ref. 1. It adds diffusion strictly in the direction orthogonal to the streamline direction. Compared to the do Carmo and Galeão formulation, the Codina formulation adds less diffusion but is not as efficient at reducing over- and undershoots. It also does not work as well for anisotropic meshes. The advantage is that the resulting nonlinear system is easier to converge and that underresolved gradients are less smeared out.

Danckwerts Inflow Boundary Condition

Constraining the composition to fixed values at an inlet to a reactor may sometimes result in issues with unreasonably high reaction rates or singularities at the inlet boundary. These problems may many times be mitigated by using a flux boundary condition instead, based on the upstream concentrations and the fluid velocity at the boundary. In chemical engineering, this type of flux boundary condition is also known as a Danckwerts condition.

Use the Danckwerts condition to specify inlet conditions for domains where high reaction rates are anticipated in the vicinity to the inlet (Ref. 2).

Given an upstream concentration $c_{i,0}$, the Danckwerts inflow boundary condition prescribed the total flux as

$$\mathbf{n} \cdot (\mathbf{J}_i + \mathbf{u}c_i) = \mathbf{n} \cdot (\mathbf{u}c_{i,0}) \tag{3-11}$$

Mass Balance Equation for Transport of Diluted Species in Porous Media

VARIABLY SATURATED POROUS MEDIA

The following equations for the molar concentrations, c_i, describe the transport of solutes in a variably saturated porous medium for the most general case, when the pore space is primarily filled with liquid but also contain pockets or immobile gas:

$$\frac{\partial}{\partial t}(\theta_l c_i) + \frac{\partial}{\partial t}(\rho c_{P,i}) + \frac{\partial}{\partial t}(\theta_g c_{G,i}) + \mathbf{u} \cdot \nabla c_i = \nabla \cdot [(D_{D,i} + D_{e,i})\nabla c_i] + R_i + S_i \tag{3-12}$$

On the left-hand side of Equation 3-12, the first three terms correspond to the accumulation of species within the liquid, solid, and gas phases, while the last term describes the convection due to the velocity field $\mathbf{u}$ (SI unit: m/s).

In Equation 3-12 c_i denotes the concentration of species i in the liquid (SI unit: mol/m^3), $c_{P,i}$ the amount adsorbed to solid particles (moles per unit dry weight of the solid), and $c_{G,i}$ the concentration of species i in the gas phase.

The equation balances the mass transport throughout the porous medium using the porosity ε_p, the liquid volume fraction θ_l; the dry bulk density, $\rho = (1 - \varepsilon_s)\rho_s$, and the solid phase density ρ_s.

For saturated porous media, the liquid volume fraction θ_l is equal to the porosity ε_p, but for unsaturated porous media, they are related by the saturation s as $\theta_l = \varepsilon_p s$. The resulting gas volume fraction in the case of an unsaturated porous medium is

$$\theta_g = \varepsilon_p - \theta_l = (1 - s)\varepsilon_p$$

On the right-hand side of Equation 3-12, the first term introduces the spreading of species due to mechanical mixing resulting from the porous media (dispersion), as well as from diffusion and volatilization to the gas phase. The dispersion tensor is denoted D_D (SI unit: m^2/s) and the effective diffusion by D_e (SI unit: m^2/s).

The last two terms on the right-hand side of Equation 3-12 describe production or consumption of the species; R_i is a reaction rate expression which can account for reactions in the liquid, solid, or gas phase, and S_i is an arbitrary source term, for example due to a fluid flow source or sink.

Adsorption

The time evolution of the adsorption, the solute transport to or from the solid phase, is defined by assuming that the amount of solute adsorbed to the solid, $c_{\mathrm{P},i}$, is a function of the concentration in the fluid c_i. This implies that the solute concentration in the liquid and solid phase are in instant equilibrium. The adsorption term can be expanded to give

$$\frac{\partial}{\partial t}(\rho c_{\mathrm{P},i}) = \rho\frac{\partial c_{\mathrm{P},i}}{\partial c_i}\frac{\partial c_i}{\partial t} - c_{\mathrm{P},i}\rho_s\frac{\partial \varepsilon_p}{\partial t} = \rho K_{\mathrm{P},i}\frac{\partial c_i}{\partial t} - c_{\mathrm{P},i}\rho_s\frac{\partial \varepsilon_p}{\partial t} \quad (3\text{-}13)$$

where $k_{\mathrm{P},i} = \partial c_{\mathrm{P},i}/\partial c_i$ is the adsorption isotherm.

Volatilization

Volatilization is the process where a solute species in the liquid is transported to the gas phase due to vaporization. Assuming that the amount of solute in the gas phase, $c_{\mathrm{G},i}$, is a linear function of the liquid phase concentration, the volatilization term is defined as

$$\frac{\partial}{\partial t}\theta_g c_{\mathrm{G},i} = \theta_g\frac{\partial c_{\mathrm{G},i}}{\partial c_i}\frac{\partial c_i}{\partial t} + k_{\mathrm{G},i}c_i\frac{\partial \theta_g}{\partial t} = \theta_g k_{\mathrm{G},i}\frac{\partial c_i}{\partial t} + k_{\mathrm{G},i}c_i\frac{\partial \theta_g}{\partial t} \quad (3\text{-}14)$$

where $k_{\mathrm{G},i} = \partial c_{\mathrm{G},i}/\partial c_i$ is the linear volatilization.

SATURATED POROUS MEDIA

In the case of transport in a saturated porous medium, $\theta_l = \varepsilon_p$, and the governing equations are

$$\frac{\partial}{\partial t}(\varepsilon_p c_i) + \frac{\partial}{\partial t}(\rho c_{\mathrm{P},i}) + \mathbf{u}\cdot\nabla c_i = \nabla\cdot[(D_{\mathrm{D},i} + D_{\mathrm{e},i})\nabla c_i] + R_i + S_i \quad (3\text{-}15)$$

Convection in Porous Media

Convection (also called advection) describes the movement of a species, such as a pollutant, with the bulk fluid velocity. The velocity field **u** corresponds to a superficial volume average over a unit volume of the porous medium, including both pores and matrix. This velocity is sometimes called *Darcy velocity*, and defined as volume flow

rates per unit cross section of the medium. This definition makes the velocity field continuous across the boundaries between porous regions and regions with free flow.

	The velocity field to be used in the Model Inputs section on the physics interface can, for example, be prescribed using the velocity field from a Darcy's Law or a Brinkman Equations interface.

The average linear fluid velocities $\mathbf{u}_a$, provides an estimate of the fluid velocity within the pores:

$$\mathbf{u}_a = \frac{\mathbf{u}}{\varepsilon_p} \quad \text{Saturated}$$

$$\mathbf{u}_a = \frac{\mathbf{u}}{\theta_l} \quad \text{Unsaturated}$$

where ε_p is the porosity and $\theta_l = s\varepsilon_p$ the liquid volume fraction, and s the saturation, a dimensionless number between 0 and 1.

Figure 3-1: A block of a porous medium consisting of solids and the pore space between the solid grains. The average linear velocity describes how fast the fluid moves within the pores. The Darcy velocity attributes this flow over the entire fluid-solid face.

CONVECTIVE TERM FORMULATION

The Transport of Diluted Species in Porous Media interface includes two formulations of the convective term. The conservative formulation of the species equations in Equation 3-12 is written as:

$$\frac{\partial}{\partial t}(\theta_l c_i) + \frac{\partial}{\partial t}(\rho c_{P,i}) + \frac{\partial}{\partial t}(\theta_g c_{G,i}) + \nabla \cdot \mathbf{u} c_i = \nabla \cdot [(D_{D,i} + D_{e,i})\nabla c_i] + R_i + S_i \quad (3\text{-}16)$$

If the conservative formulation is expanded using the chain rule, then one of the terms from the convection part, $c_i \nabla \cdot \mathbf{u}$, would equal zero for an incompressible fluid and would result in the nonconservative formulation described in Equation 3-12.

When using the nonconservative formulation, which is the default, the fluid is assumed incompressible and divergence free: $\nabla \cdot \mathbf{u} = 0$. The nonconservative formulation improves the stability of systems coupled to a momentum equation (fluid flow equation).

To switch between the two formulations, click the **Show** button ( ) and select **Advanced Physics Options**. In the section **Advanced Settings** select either **Nonconservative form** (the default) or **Conservative form**. The conservative formulation should be used for compressible flow.

Diffusion in Porous Media

The effective diffusion in porous media, D_e, depends on the structure of the porous material and the phases involved. Dependent on whether the transport of diluted species occurs in free flow, saturated or unsaturated porous media, the effective diffusivity is defined as:

$$D_e = D_F \quad \text{Free Flow}$$

$$D_e = \frac{\varepsilon_p}{\tau_L} D_L \quad \text{Saturated Porous Media}$$

$$D_e = \frac{\theta_l}{\tau_L} D_L \quad \text{Unsaturated Porous Media}$$

$$D_e = \frac{\theta_l}{\tau_L} D_L + \frac{\theta_g}{\tau_G} k_G D_G \quad \text{Unsaturated with Volatilization}$$

Here D_F, D_L, and D_G are the single-phase diffusion coefficients for the species diluted in a fluid, a pure liquid, and a gas phase, respectively (SI unit: m^2/s), and τ_F, τ_L, and τ_G are the corresponding tortuosity factors (dimensionless).

The tortuosity factor accounts for the reduced diffusivity due to the fact that the solid grains impede Brownian motion. The interface provides predefined expressions to

compute the tortuosity factors in partially saturated porous media according to the Millington and Quirk model (Ref. 12):

$$\tau_L = \theta_l^{-7/3}\varepsilon_p^{\,2},\ \tau_G = \theta_g^{-7/3}\varepsilon_p^{\,2}$$

and Bruggeman model

$$\tau_L = \theta_l^{-5/2}\varepsilon_p^{\,2},\ \tau_G = \theta_g^{-5/2}\varepsilon_p^{\,2}$$

For saturated porous media $\theta_l = \varepsilon_p$. The fluid tortuosity for the Millington and Quirk model is

$$\tau_L = \varepsilon_p^{-1/3}$$

and for the Bruggeman model the tortuosity is defined as

$$\tau_L = \varepsilon_p^{-1/2}$$

User defined expressions for the tortuosity factor can also be applied.

Dispersion

The contribution of dispersion to the mixing of species typically overshadows the contribution from molecular diffusion, except when the fluid velocity is very small.

The spreading of mass, as a fluid travel through a porous medium is caused by several contributing effects. Local variations in fluid velocity lead to mechanical mixing referred to as dispersion occurs because the fluid in the pore space flows around solid particles, so the velocity field varies within pore channels. The spreading in the direction parallel to the flow, or *longitudinal dispersivity*, typically exceeds the *transverse dispersivity* from up to an order of magnitude. Being driven by the concentration gradient alone, molecular diffusion is small relative to the mechanical dispersion, except at very low fluid velocities.

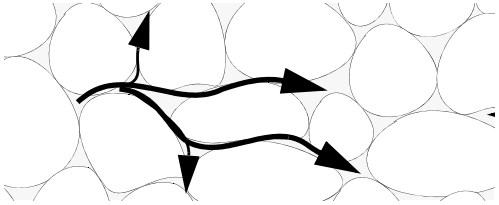


Figure 3-2: Spreading of fluid around solid particles in a porous medium.

The dispersion is controlled through the dispersion tensor D_{D}. The tensor components can either be given by user-defined values or expressions or derived from the directional dispersivities.

Using the longitudinal and transverse dispersivities in 2D, the dispersivity tensor components are (Ref. 9):

$$D_{\mathrm{D}ii} = \alpha_{\mathrm{L}}\frac{u_i^2}{|\mathbf{u}|} + \alpha_{\mathrm{T}}\frac{u_j^2}{|\mathbf{u}|}$$

$$D_{\mathrm{D}ij} = D_{\mathrm{D}ji} = (\alpha_{\mathrm{L}} - \alpha_{\mathrm{T}})\frac{u_i u_j}{|\mathbf{u}|}$$

In these equations, $D_{\mathrm{D}ii}$ (SI unit: m^2/s) are the principal components of the dispersivity tensor, and $D_{\mathrm{D}ji}$ and $D_{\mathrm{D}ji}$ are the cross terms. The parameters α_{L} and α_{T} (SI unit: m) specify the longitudinal and transverse dispersivities; and u_i (SI unit: m/s) stands for the velocity field components.

In order to facilitate modeling of stratified porous media in 3D, the tensor formulation by Burnett and Frind (Ref. 10) can be used. Consider a transverse isotropic media, where the strata are piled up in the z direction, the dispersivity tensor components are:

$$
\begin{aligned}
D_{\mathrm{L}xx} &= \alpha_1 \frac{u^2}{|\mathbf{u}|} + \alpha_2 \frac{v^2}{|\mathbf{u}|} + \alpha_3 \frac{w^2}{|\mathbf{u}|} \\
D_{\mathrm{L}yy} &= \alpha_1 \frac{v^2}{|\mathbf{u}|} + \alpha_2 \frac{u^2}{|\mathbf{u}|} + \alpha_3 \frac{w^2}{|\mathbf{u}|} \\
D_{\mathrm{L}zz} &= \alpha_1 \frac{w^2}{|\mathbf{u}|} + \alpha_3 \frac{u^2}{|\mathbf{u}|} + \alpha_3 \frac{v^2}{|\mathbf{u}|} \\
D_{\mathrm{L}xy} &= D_{\mathrm{L}yx} = (\alpha_1 - \alpha_2) \frac{uv}{|\mathbf{u}|} \\
D_{\mathrm{L}xz} &= D_{\mathrm{L}zx} = (\alpha_1 - \alpha_3) \frac{uw}{|\mathbf{u}|} \\
D_{\mathrm{L}yz} &= D_{\mathrm{L}zy} = (\alpha_1 - \alpha_3) \frac{vw}{|\mathbf{u}|}
\end{aligned}
\tag{3-17}
$$

In Equation 3-17 the fluid velocities u, v, and w correspond to the components of the velocity field $\mathbf{u}$ in the x, y, and z directions, respectively, and α_1 (SI unit: m) is the longitudinal dispersivity. If z is the vertical axis, α_2 and α_3 are the dispersivities in the transverse horizontal and transverse vertical directions, respectively (SI unit: m). Setting $\alpha_2 = \alpha_3$ gives the expressions for isotropic media shown in Bear (Ref. 9 and Ref. 11).

Adsorption

As species travel through a porous medium they typically attach to (adsorb), and detach (desorb) from the solid phase, which slows chemical transport through the porous medium. Adsorption and desorption respectively reduces or increases species concentrations in the fluid. The adsorption properties vary between chemicals, so a plume containing multiple species can separate into components (Ref. 6). The Adsorption feature includes four predefined and one user defined relationships to predict the solid concentrations, $c_{\mathrm{P}i}$ from the concentration in the liquid phase, c_i:

$$
\begin{aligned}
c_P &= c_{P\max}\frac{K_L c}{1+K_L c} && \text{Langmuir}\\
c_P &= K_F\left(\frac{c}{c_{ref}}\right)^N && \text{Freundlich}\\
c_P &= c_{P\max}\frac{b_T c}{\left(1+(b_T c)^{N_T}\right)^{1/N_T}} && \text{Toth}\\
c_P &= \frac{K_B c_0 c}{(c_S-c)\left(1+(K_B-1)\dfrac{c}{c_S}\right)} && \text{BET}
\end{aligned}
\qquad (3\text{-}18)
$$

The above equations contains the following parameters:

- Freundlich: Freundlich constant K_F (SI unit:·mol/kg), Freundlich exponent N_F (dimensionless), and reference concentration c_{ref} (SI unit: mol/m^3).
- Langmuir: Langmuir constant K_L (SI unit: m^3/mol), and adsorption maximum c_{Pmax} (SI unit: mol/kg).
- Toth: Toth constant b_T (SI unit: m^3/mol), Toth exponent N_T (dimensionless), and adsorption maximum c_{Pmax} (SI unit: mol/kg).
- BET (Braunauer-Emmett-Teller): BET constant K_B (dimensionless), and a monolayer adsorption capacity c_0 (SI unit: mol/kg) and a Saturation concentration, c_S(SI unit: mol/m^3).

These predefined expressions are adsorption isotherms that describe the amount of species sorbed to the solid. Defined at equilibrium, the switch between liquid and solid phases is instantaneous.

Using a Species Source feature, arbitrary expressions can be entered to define, for example, nonequilibrium and temperature-dependent adsorption laws, including those set out by Fetter (Ref. 7) and Bear and Verruijt (Ref. 8).

The retardation factor, RF, describes how adsorption slows the solute velocity, $\mathbf{u}_c$, relative to the average linear velocity of the fluid, $\mathbf{u}_a$, as in

$$
RF = 1+\frac{\rho_b}{\theta}\frac{\partial c_P}{\partial c} = \frac{\mathbf{u}_a}{\mathbf{u}_c}
$$

If the contaminant moves at the average linear velocity of the fluid for $RF = 1$. For $RF > 1$, the contaminant velocity is smaller than the fluid velocity owing to residence time on solids.

Reactions

Chemical reactions of all types influence species transport in porous media. Examples include biodegradation, radioactive decay, transformation to tracked products, temperature- and pressure-dependent functions, exothermic reactions, and endothermic reactions. The reactions represent change in species concentration per unit volume porous medium per time. Reaction terms are used on the right-hand side of the governing equation to represent these processes. For reactions in a fluid phase, multiply the expression by the fluid volume fraction θ. Similarly, solid phase reaction expressions include the bulk density, ρ_b, and gas phase reactions include the gas volume fraction, a_v.

The following expressions define some common types of reactions:

$$R_{Li} = -\theta\frac{\ln 2}{\lambda_{Li}}c_i \qquad \text{Radioactive decay — liquid}$$

$$R_{Pi} = -\rho_b\frac{\ln 2}{\lambda_{Pi}}\left(\frac{\partial c_{Pi}}{\partial c_i}\right)c_i \qquad \text{Radioactive decay — solid}$$

$$R_{Gi} = -\frac{\ln 2}{\lambda_{Gi}}a_v\left(\frac{\partial c_{Gi}}{\partial c}\right)c_i \qquad \text{Radioactive decay — gas}$$

$$R_{Lk} = \theta\zeta_{Li}c_i \qquad \text{Creation from parent } c_{Li} \text{ — liquid}$$

$$R_{Pk} = \rho_b\zeta_{Pi}\left(\frac{\partial c_{Pi}}{\partial c_i}\right)c_i \qquad \text{Creation from sorbed parent } c_{Pi} \text{ — solid}$$

$$R_{Gk} = -\zeta a_v\left(\frac{\partial c_{Gi}}{\partial c}\right)c_i \qquad \text{Reaction — gas}$$

where λ is the chemical half life, ζ is a reaction rate, and the subscripts L, P, and G denote liquid, solid, and gas phases, respectively. In the equations, the reactions either depend on liquid concentration c_i or solid phase concentrations c_{Pi} obtained using the sorption derivative with c_i or gas phase concentration c_{Gi} depending on the gas volume fraction, the volatilization, and the liquid concentration.

Reaction rates can vary with results from other equations in your model, such as temperature. For example, enter the Arrhenius rate law given in Ref. 13:

$$\zeta_T = \zeta_R \exp\left[\frac{E_a(T - T_R)}{R_u T T_R}\right] \tag{3-19}$$

In Equation 3-19, T denotes the current absolute temperature, T_R denotes the reference absolute temperature, E_a is the activation energy, and R_u is the universal gas constant.

Mass Transport in Fractures

When thin fractures occur in porous media, fluid flow tends to move faster along the fracture than in the surrounding media. The transport of chemical species therefore also occur also faster in the direction of the fractures.

The fluid flow in a fracture can be modeled using Darcy's law formulated in a thin sheet of porous medium (a fracture):

$$\mathbf{u} = \frac{\kappa}{\mu}\nabla_t p$$

Here $\mathbf{u}$ is the tangential Darcy velocity, κ is the fracture permeability, μ the fluid's dynamic viscosity, and $\nabla_t p$ is the tangential gradient of the fluid pressure.

The equation to solve for mass transport of species c_i in a thin fracture, embedded in a porous media, is derived from Equation 3-12. The resulting equation is:

$$d_{\mathrm{fr}}\left(\frac{\partial \rho_b c_{\mathrm{P},i}}{\partial t} + \frac{\partial \varepsilon_p c_i}{\partial t} + \nabla_t \cdot (D_{\mathrm{e},i}\nabla_t c_i) + \mathbf{u}\cdot\nabla_t c_i\right) = d_{\mathrm{fr}}R_i + d_{\mathrm{fr}}S_i + n_0 \qquad (3\text{-}20)$$

Here d_{fr} is the fracture thickness, $c_{\mathrm{P},i}$ the amount of species adsorbed to (or desorbed from) the porous matrix (moles per unit dry weight of the solid), ε_p is the fracture porosity, and D_e is the effective diffusivity. The first two terms on the right hand side represent source terms from reactions, and n_0 corresponds to out-of plane flux from the adjacent porous domain.

In order to arrive at the tangential differential equation, the gradient is split into the contributions normal and tangential to the fracture:

$$\nabla c_i = \nabla_n c_i + \nabla_t c_i$$

The normal gradient is defined in the direction normal to the boundary representing the fracture and the tangential gradient is defined along the boundary. Assuming that the variations in the normal (thin) direction of the fracture are negligible compared to those in the tangential direction, the gradient is simplified as:

$$\nabla c_i = \nabla_t c_i$$

Using The Transport of Diluted Species in Fractures Interface, the transport along fracture boundaries alone is solved for. In this case the transport in the surrounding porous media neglected and the out-of plane flux n_0 vanishes.

See Fracture for more information about the boundary feature solving Equation 3-20. See The Transport of Diluted Species in Fractures Interface for more information about the physics interface solving the equation on boundaries only.

Theory for the Reactive Pellet Bed

The Reactive Pellet Bed, available to users of the Chemical Reaction Engineering Module, adds to the Transport of Diluted Species interface a domain feature that can simulate regions filled with reactive catalyst pellets, as in packed bed reactors. The pellets are simulated with the Extra Dimension technology provided by the COMSOL software: A 1D, 2D, or 3D domain represents the bed volume. The extra dimension is the added radial microscale dimension inside each pellet.

For an example of how to use the Reactive Pellet Bed, see the model example *A Multiscale 3D Packed Bed Reactor*, file path **Chemical_Reaction_Engineering_Module/Reactors_with_Porous_Catalysts/packed_bed_reactor_3d**

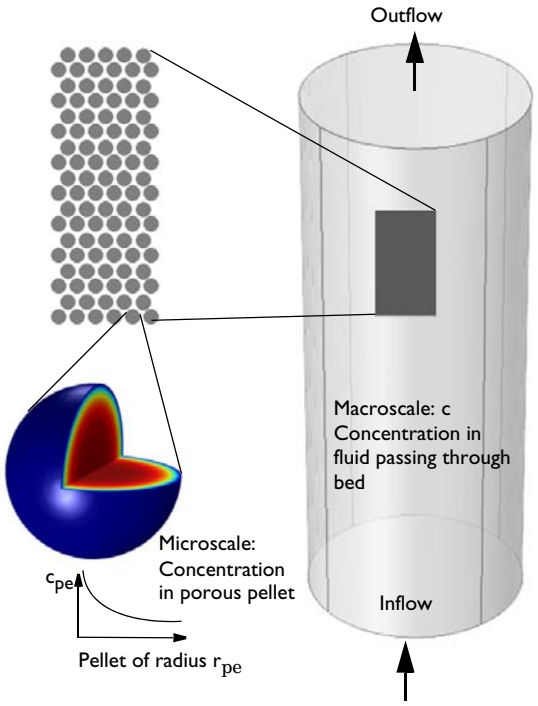


Figure 3-3: Schematic showing the macroscale (bed volume) and the microscale (pellet).

The transport and reaction equations inside the pellets are solved on an extra dimension attached to the 1D, 2D, or 3D physics interfaces, including axisymmetric cases.

The equations inside the spherical pellet are solved as a spherical transport equations on a nondimensional radial coordinate on the domain 0-1. A given pellet size or a discrete distribution of sizes can be used.

The model equations assume spherical particles (pellets) of a radius r_{pe}. Modeling assumptions for cylinders, flakes, and user-defined shapes can also be used. Consider the microscale concentration c_{pe} inside an individual porous pellet or pellets, and the macro-concentration c in the packed bed gas volume.

The pellet radius input can be:

- One uniform pellet radius, which can be space dependent $f(x, y, z)$.
- Binary, ternary, and so on, mix up to 5 radii. The user inputs a table with the mix of sizes (1 mm, 2 mm, for example), and a volume fraction of each. Different chemical reactions per pellet size can be specified.

The model equation for the bulk (macroscale) species is, for example:

$$\varepsilon_b \frac{\partial}{\partial t}(c_i) + \mathbf{u} \cdot \nabla c_i + \nabla \cdot (-D_{b,i} \nabla c_i) = R_i \qquad (3\text{-}21)$$

- ε_b is the bed porosity.
- The dependent variable c for each chemical species i represents the interstitial concentration, that is, the physical concentration based on unit volume of fluid flowing between the pellets.
- R_i is the species reaction rate in the bed. This corresponds to reactions occurring in the pore space outside of the pellets. Note, that R_i is the reaction rate per unit volume of bed.

Looking inside a pellet: Assuming no concentration variations in the space-angle (θ, φ) direction, but only in the radial (r) direction of the spherical pellet allows a spherically symmetric reaction-diffusion transport equation inside the pellet. If r_{dim} (SI unit: m) is the spatial radial coordinate in the pellet, and r_{pe} is the pellet radius, the nondimensional coordinate $r = r_{dim}/r_{pe}$ can be defined. The modeling domain on r goes from 0 to 1.

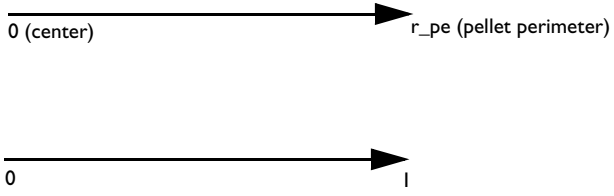


Figure 3-4: Modeling domain in a pellet for dimensional (top) and nondimensional (bottom) coordinates.

A shell mole balance across a spherical shell at radius r_{dim} (SI unit: m), and a subsequent variable substitution $r = r_{\text{dim}}/r_{\text{pe}}$ gives the following transport equation on the pellet domain $0 < r < 1$:

$$4\pi\left\{r^2 {r_{\text{pe}}}^2 \varepsilon_{\text{pe}} \frac{\partial}{\partial t}(c_{\text{pe},i}) + \nabla \cdot (-r^2 D_{\text{pe},i} \nabla c_{\text{pe},i}) = r^2 {r_{\text{pe}}}^2 R_{\text{pe},i}\right\} \tag{3-22}$$

- ε_{pe} is the pellet (microscale) porosity.
- As in Equation 3-22, c_{pe} is the interstitial (physical) species concentration in moles/m^3 of fluid volume element inside the pore channel.
- $R_{\text{pe,i}}$ is the pellet reaction rate. This corresponds to reactions taking place inside the pellets. Note that the user input of $R_{\text{pe},i}$ is per unit volume of pellet.

Assuming that the pellets bed is homogenized, that is that pellets are present in an averaged sense in each point of the geometry, the equation to be solved in the reactive bed is:

$$4\pi N\left\{r^2 {r_{\text{pe}}}^2 \varepsilon_{\text{pe}} \frac{\partial}{\partial t}(c_{\text{pe},i}) + \nabla \cdot (-r^2 D_{\text{pe},i} \nabla c_{\text{pe},i}) = r^2 {r_{\text{pe}}}^2 R_{\text{pe},i}\right\} \tag{3-23}$$

where N is the number of pellets per unit volume of bed:

$$N = \frac{(1-\varepsilon_{\text{b}})}{V_{\text{pe}}}$$

Dividing Equation 3-22 with the pellet by $4\pi r^2 {r_{\text{pe}}}^2$ (the pellet area times r^2), the governing equation inside the each pellet is:

$$\varepsilon_{\text{pe}} \frac{\partial}{\partial t}(c_{\text{pe},i}) + \frac{a}{r^2 {r_{\text{pe}}}^2} \nabla \cdot (-r^2 D_{\text{pe},i} \nabla c_{\text{pe},i}) = R_{\text{pe},i} \tag{3-24}$$

The effective diffusion coefficient in the equations above depends on the porosity ε_{pe}, tortuosity τ, and physical gas diffusivity D in the manner of

$$D_{\text{pe}} = \frac{\varepsilon_{\text{pe}} D}{\tau}.$$

The available models for the porous media tortuosity are the one by Millington and Quirk (Ref. 12),

$$\tau = {\varepsilon_{\text{pe}}}^{-1/3} \Rightarrow D_{\text{pe}} = {\varepsilon_{\text{pe}}}^{4/3} D\,, \tag{3-25}$$

the Bruggeman model,

$$\tau = \varepsilon_{pe}^{-1/2} \Rightarrow D_{pe} = \varepsilon_{pe}^{3/2} D \tag{3-26}$$

and the Tortuosity model, where the tortuosity expression is entered as user defined input.

These are readily used for both gaseous and liquid fluids along with various types of pellet shapes. For instance, the first model has been shown to fit mass transport in soil-vapor and soil-moisture well.

Equation 3-22 can be solved for two types of boundary conditions at the interface between the pellet surface and the fluid in this feature.

- **Continuous concentration:** assuming that all resistance to mass transfer to/from the pellet is within the pellet and no resistance to pellet-fluid mass transfer is on the bulk fluid side. The concentration in the fluid will thus be equal to that in the pellet pore just at the pellet surface: $c_{pe,i} = c_i$. This constraint also automatically ensures flux continuity between the internal pellet domain and the free fluid domain through so-called reaction forces in the finite element formulation.
- **Film resistance (mass flux):** The flux of mass across the pellet-fluid interface into the pellet is possibly rate determined on the bulk fluid side by film resistance. The resistance is expressed in terms of a film mass transfer coefficient, h_{Di}, such that:

$$N_{i,\text{inward}} = h_{D,i}(c_i - c_{pe,i}), \tag{3-27}$$

  where $N_{i,\text{inward}}$ is the molar flux from the free fluid into a pellet and has the unit moles/(m^2·s).

With the film resistance formulation above, the free fluid Equation 3-21 needs to be amended for flux continuity so that

$$\varepsilon_b \frac{\partial}{\partial t}(c_i) + \mathbf{u} \cdot \nabla c_i + \nabla \cdot (-D_{b,i} \nabla c_i) = R_i - N_{i,\text{inward}} S_b \tag{3-28}$$

where S_b (SI unit: m^2/m^3) is the specific surface area exposed to the free fluid of the packed bed (not including the inside of the pores).

For the case of randomly packed spherical pellets, the specific surface area exposed to the free fluid is (Ref. 3):

$$S_b = \frac{3}{r_{pe}}(1 - \varepsilon_b) \tag{3-29}$$

The mass transfer coefficient in Equation 3-27 can be computed from the fluid properties and flow characteristics within the porous media. For this, the Sherwood, Sh, number defined as the ratio between the convective mass transfer coefficient and the diffusive mass transfer coefficient is often used:

$$\mathrm{Sh} = \frac{hL}{D}$$

where L is a characteristic length (for spheres, typically the radius), and D is the diffusion coefficient in the fluid. From the Sherwood number definition, the mass transfer coefficient can be computed.

Three commonly used empirical expressions for the calculation of the Sherwood number are the Frössling relation (Ref. 4):

$$\mathrm{Sh} = 2 + 0.552\mathrm{Re}^{1/2}\mathrm{Sc}^{1/3}, \tag{3-30}$$

which was measured on pellets in the size region 1 mm, the Rosner relation (Ref. 5)

$$\mathrm{Sh} = \mathrm{Sc}^{0.4}(0.4\mathrm{Re}^{1/2} + 0.2\mathrm{Re}^{2/3}), \tag{3-31}$$

and the Garner and Keey relation (Ref. 4)

$$\mathrm{Sh} = 0.94\mathrm{Re}^{1/2}\mathrm{Sc}^{1/3}, \tag{3-32}$$

which was measured for Re numbers greater than 250.

All three depend on the Reynolds, Re, and Schmidt, Sc, numbers. The first describing the fluid flow regime (laminar versus turbulent) and the second, the ratio between the viscous diffusion rate and the molecular (mass) diffusion rate. In the expressions, properties such as velocity, u, dynamic viscosity, μ, and density, ρ, of the fluid are included.

$$\mathrm{Re} = \frac{\rho u L}{\mu}$$

$$\mathrm{Sc} = \frac{\mu}{\rho D}$$

SURFACE SPECIES

Surface species correspond to species bound to the solid interface within the porous pellet, which is also in contact with the pore fluid. The surface species hence only exists within the pellet. The surface species are assumed to be immobile, and the

concentration is only dependent on the reaction rate of surface reactions involving the species:

$$\frac{\partial c_{\text{pes}}}{\partial t} = R^s_{\text{pes}} \tag{3-33}$$

It can be noted that there is no mass flux of surface species within the pellet or across the pellet outer surface and the bulk fluid. The unit of surface species concentration c_{pes} is amount per area, and the corresponding surface reaction rate unit is amount per area and time.

When surface species are present, the equation governing transport of bulk species inside the each pellet is:

$$\varepsilon_{\text{pe}}\frac{\partial}{\partial t}(c_{\text{pe},i}) + \frac{a}{r^2 r_{\text{pe}}^2}\nabla \cdot (-r^2 D_{\text{pe},i}\nabla c_{\text{pe},i}) = R_{\text{pe},i} + S_{\text{b,reac}}R^s_{\text{pe}} \tag{3-34}$$

The second term on the right hand side represents species production or removal due to surface reactions in the pellet. It is composed of the reactive specific area $S_{\text{b,reac}}$, the area per volume available for surface reactions, and the surface reaction rate R^s_{pe}.

It should be noted that the surface reaction rate for a bulk species R^s_{pe} and the surface reaction rate for a surface species R^s_{pes} are related but not identical since the species may represent different molecules.

NONSPHERICAL PARTICLES

For nonspherical pellets (of any shape), the relations above can be applied approximately by reinterpreting the pellet radius r_{pe} as

$$r_{\text{pe}} = 3\frac{V_{\text{pe}}}{A_{\text{pe}}} \tag{3-35}$$

(Ref. 14), where V_{pe} and A_{pe} are the volume and external surface, respectively, of a single pellet of any shape. Since the specific surface S_{pe} (SI unit: m^2/m^3) of one pellet is defined as

$$S_{\text{pe}} = \frac{A_{\text{pe}}}{V_{\text{pe}}}$$

it follows by insertion of Equation 3-35 that

$$S_{pe} = \frac{3}{r_{pe}}.$$

For a packed bed of which the packing has a porosity ε_b, the specific surface of the bed will be

$$S_b = S_{pe}(1-\varepsilon_b) = \frac{A_{pe}}{V_{pe}}(1-\varepsilon_b)$$

or

$$S_b = \frac{3}{r_{pe}}(1-\varepsilon_b) \tag{3-36}$$

for any pellet shape. Now r_{pe} and S_b can be calculated for any shape and inserted in equations Equation 3-22 and Equation 3-28. Some common specific shapes have automatic support:

Cylinders

For cylindrical shapes, applying Equation 3-35 gives

$$r_{pe} = 3\frac{V_{pe}}{A_{pe}} = 3\frac{\pi r_{cyl}^2 L_{cyl}}{2\pi r_{cyl}L_{cyl} + 2\pi r_{cyl}^2} = \frac{1}{\frac{2}{3r_{cyl}} + \frac{2}{3L_{cyl}}}. \tag{3-37}$$

It is common practice to assume that the top and bottom surface of cylindrical pellets have negligible effect on the mass transfer to and from the internals of the pellet, or, $r_{cyl} \ll L_{cyl}$. Equation 3-37 then simplifies to

$$r_{pe} = \frac{3}{2}r_{cyl}$$

and Equation 3-36 to

$$S_b = \frac{2}{r_{cyl}}(1-\varepsilon_b)$$

Flakes

The derivation for a disc-shaped catalyst pellet is exactly the same as for cylindrical pellets, except that the assumption is reversed about the end surfaces and the envelope surface: $r_{flake} \gg w_{flake}$, where w_{flake} is the thickness of the disc. This gives

$$r_{\text{pe}} = \frac{3}{2} w_{\text{flake}}$$

and

$$S_{\text{b}} = \frac{2}{w_{\text{flake}}} (1 - \varepsilon_{\text{b}}) .$$

SURFACE REACTION

Surface reactions can also be simulated inside the pellet. Surface species are introduced into pellet by adding them in the Surface Species section of the Reactive Pellet Bed feature.

A bulk species can take part in both volumetric and surface reactions. The total reaction rate for a bulk species within a pellet is defined as:

$$R = R_{\text{pe}} + R_{\text{pe,s}} \cdot S_{\text{b,reac}}$$

Here R_{pe} is the reaction rate for bulk reactions occurring inside the pellet. $R_{\text{pe,s}}$ and S_{b} are the reaction rate and the reactive specific surface area for a surface reaction occurring inside the pellet, on the interface between the solid matrix and the fluid.

HEAT SOURCE

The heat source of endothermic or exothermic reactions inside the pellet needs to be accounted for in the heat transfer on the bulk level if the heat balance is not solved within the pellet. Thermal equilibrium is assumed in each pellet, and the source is averaged across the pellet:

$$Q_{\text{bed}} = \frac{\int_V Q_{\text{pe}} dV}{V_{\text{pe}}} (1 - \varepsilon_{\text{b}}) \ (\text{W/m}^3)$$

If there are multiple pellet sizes i in the bed the heat source computed by summing over all sizes:

$$Q_{\text{bed}} = \sum_i (Q_{\text{bed},\, i} \cdot \theta_{\text{v},i})$$

Here $\theta_{\text{v,i}}$ is the volume fraction of pellet i in the pellet mix.

References

1. R. Codina, "A discontinuity-capturing crosswind-dissipation for the finite element solution of the convection-diffusion equation", *Computer Methods in Applied Mechanics and Engineering*, vol. 110, pp. 325–342, 1993.

2. P.V. Danckwerts, "Continuous flow systems: Distribution of residence times", *Chem. Eng. Sci.*, vol. 2, no. 1, 1953.

3. J.M. Coulson and J.F. Richardson, *Chemical Engineering, vol. 2*, 4th ed., Pergamon Press, Oxford, U.K., 1991.

4. J.M. Coulson and J.F. Richardson, *Chemical Engineering, vol. 1*, 4th ed., Pergamon Press, Oxford, U.K., 1991.

5. D.E Rosner, *Transport Processes in Chemically Reacting Flow Systems*, ISBN-13: 978-1483130262, Butterworth-Heinemann, 1986.

6. D.M. Mackay, D.L. Freyberg, P.V. Roberts, and J.A. Cherry, "A Natural Gradient Experiment on Solute Transport in a Sand Aquifer: 1. Approach and Overview of Plume Movement", *Water Resourc. Res.*, vol. 22, no. 13, pp. 2017–2030, 1986.

7. C.W. Fetter, *Contaminant Hydrogeology*, Prentice Hall, 1999.

8. J. Bear and A. Verruijt, *Modeling Groundwater Flow and Pollution*, D. Reidel Publishing, 1994.

9. J. Bear, *Hydraulics of Groundwater*, McGraw-Hill, 1979.

10. R.D. Burnett and E.O. Frind, "An Alternating Direction Galerkin Technique for Simulation of Groundwater Contaminant Transport in Three Dimensions: 2. Dimensionality Effects", *Water Resour. Res.*, vol. 23, no. 4, pp. 695–705, 1987.

11. J. Bear, *Dynamics of Fluids in Porous Media*, Elsevier Scientific Publishing, 1972.

12. R.J. Millington and J.M. Quirk, "Permeability of Porous Solids", *Trans. Faraday Soc.*, vol. 57, pp. 1200–1207, 1961.

13. I. Langmuir, "Chemical Reactions at Low Temperatures", *J. Amer. Chem. Soc.*, vol. 37, 1915.

14. R.B. Bird, W.E. Stewart, and E.N. Lightfoot, *Transport Phenomena*, 2nd ed., John Wiley & Sons, Inc., 2007.

Theory for the Transport of Concentrated Species Interface

The Transport of Concentrated Species Interface theory is described in this section:

- Multicomponent Mass Transport
- Multicomponent Gas Diffusion: Maxwell–Stefan Description
- Multicomponent Diffusivities
- Multicomponent Diffusion: Mixture-Averaged Approximation
- Multispecies Diffusion: Fick's Law Approximation
- Multicomponent Thermal Diffusion
- Reactive Pellet Bed
- Regularization of Reaction Rate Expression
- References for the Transport of Concentrated Species Interface

Multicomponent Mass Transport

Suppose a reacting flow consists of a mixture with $i = 1, \ldots, Q$ species and $j = 1, \ldots, N$ reactions. Equation 3-121 then describes the mass transport for an individual species:

$$\frac{\partial}{\partial t}(\rho\omega_i) + \nabla \cdot (\rho\omega_i \mathbf{u}) = -\nabla \cdot \mathbf{j}_i + R_i \tag{3-38}$$

where, ρ (SI unit: kg/m^3) denotes the mixture density and $\mathbf{u}$ (SI unit: m/s) the mass averaged velocity of the mixture. The remaining variables are specific for each of the species, i, being described by the mass transfer equation:

- ω_i is the mass fraction (1)
- $\mathbf{j}_i$ (SI unit: kg/(m^2·s)) is the mass flux relative to the mass averaged velocity, and
- R_i (SI unit: kg/ (m^3·s)) is the rate expression describing its production or consumption.

The relative mass flux vector $\mathbf{j}_i$ can include contributions due to molecular diffusion, mass flux due to migration in an electric field, and thermal diffusion.

Summation of the transport equations over all present species gives Equation 3-39 for the conservation of mass

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \tag{3-39}$$

assuming that

$$\sum_{i=1}^{Q} \omega_i = 1, \quad \sum_{i=1}^{Q} \mathbf{j}_i = 0, \quad \sum_{i=1}^{Q} R_i = 0$$

Using the mass conservation equation, the species transport for an individual species, i, is given by:

$$\rho \frac{\partial}{\partial t}(\omega_i) + \rho(\mathbf{u} \cdot \nabla)\omega_i = -\nabla \cdot \mathbf{j}_i + R_i \tag{3-40}$$

$Q - 1$ of the species equations are independent and possible to solve for using Equation 3-40. To compute the mass fraction of the remaining species, COMSOL Multiphysics uses the fact that the sum of the mass fractions is equal to 1:

$$\omega_1 = 1 - \sum_{i=2}^{Q} \omega_i \tag{3-41}$$

Multicomponent Gas Diffusion: Maxwell–Stefan Description

In a multicomponent mixture, the mass flux relative to the mass average velocity, $\mathbf{j}_i$, can be defined by the generalized Fick equations (Ref. 1):

$$\mathbf{j}_i = -\rho \omega_i \sum_{k=1}^{Q} \tilde{D}_{ik} \mathbf{d}_k - D_i^T \nabla \ln T \tag{3-42}$$

In Equation 3-42:

- $\tilde{D}_{ik}$ (SI unit: m^2/s) are the multicomponent Fick diffusivities
- T (SI unit: K) is the temperature
- D_i^T (SI unit: kg/ m·s)) are the thermal diffusion coefficients, and
- $\mathbf{d}_k$ (SI unit: 1/m) is the diffusional driving force acting on species k.

For ideal gas mixtures the diffusional driving force is (Ref. 1)

$$\mathbf{d}_k = \frac{1}{cR_gT}\left[\nabla p_k - \omega_k \nabla p - \rho_k \mathbf{g}_k + \omega_k \sum_{l=1}^{Q} \rho_l \mathbf{g}_l\right] \tag{3-43}$$

where

- c (SI unit: mol/m^3) is the total molar concentration
- R_g is the universal gas constant 8.314 J/(mol·K)
- p (SI unit: Pa) is the total pressure
- p_k (SI unit: Pa) is the partial pressure, and
- ρ_k (SI unit: kg/m^3) is the density of species k, and
- $\mathbf{g}_k$ (SI unit: m/s^2) is an external force (per unit mass) acting on species k. In the case of an ionic species the external force arises due to the electric field.

As can be seen in Equation 3-42 and Equation 3-43, the total diffusive flux for the species depends on the gradients of all species concentrations, temperature, and pressure as well as any external force on the individual species.

Using the ideal gas law, $p = c \cdot R_g \cdot T$, and the definition of the partial pressures, $p_k = x_k p$, the equation can be written as

$$\mathbf{d}_k = \nabla x_k + \frac{1}{p}\left[(x_k - \omega_k)\nabla p - \rho\omega_k \mathbf{g}_k + \omega_k \sum_{l=1}^{Q} \rho\omega_l \mathbf{g}_l\right] \tag{3-44}$$

The mole fraction x_k is given by

$$x_k = \frac{\omega_k}{M_k} M \tag{3-45}$$

and the mean molar mass M (SI unit: kg/mol) by

$$\frac{1}{M} = \sum_{i=1}^{Q} \frac{\omega_i}{M_i}$$

When using the Maxwell–Stefan diffusion model, the transport equations for the species' mass are

$$\rho\frac{\partial}{\partial t}(\omega_i) + \rho(\mathbf{u}\cdot\nabla)\omega_i = \nabla\cdot\left(\rho\omega_i\sum_{k=1}^{Q}\tilde{D}_{ik}\mathbf{d}_k + D_i^T\frac{\nabla T}{T}\right) + R_i$$
$$\mathbf{d}_k = \nabla x_k + \frac{1}{p}\left[(x_k-\omega_k)\nabla p - \rho\omega_k\mathbf{g}_k + \omega_k\sum_{l=1}^{Q}\rho\omega_l\mathbf{g}_l\right] \quad (3\text{-}46)$$

Multicomponent Diffusivities

The multicomponent Fick diffusivities, $\tilde{D}_{ik}$, are needed to solve Equation 3-46. The diffusivities are symmetric

$$\tilde{D}_{ik} = \tilde{D}_{ki}$$

and are related to the multicomponent Maxwell–Stefan diffusivities, D_{ik}, through the following relation (Ref. 2)

$$\frac{x_i x_k}{D_{ik}} = -\omega_i\omega_k\frac{\sum_{j\neq i}(\mathrm{adj}B_i)_{jk}}{\sum_{j\neq i}\tilde{D}_{ij}(\mathrm{adj}B_i)_{jk}},\quad (B_i)_{kj} = \tilde{D}_{kj} - \tilde{D}_{ij},\qquad i\neq j \quad (3\text{-}47)$$

where $(\mathrm{adj}B_i)_{jk}$ is the jk^{th} component of the adjoint of the matrix B_i.

For low-density gas mixtures, the multicomponent Maxwell–Stefan diffusivities, D_{ij}, can be replaced with the binary diffusivities for the species pairs that are present.

Solving for Equation 3-47 leads to a number of algebraic expressions for each of the components in the multicomponent Fick diffusivity matrix. For two- and three-component systems, these are implemented and solved directly by COMSOL Multiphysics. For instance, the component $\tilde{D}_{12}$ in a ternary system is given by:

$$\tilde{D}_{12} = \frac{-\dfrac{\omega_1(\omega_2+\omega_3)}{x_1 D_{23}} - \dfrac{\omega_2(\omega_1+\omega_3)}{x_2 D_{13}} + \dfrac{\omega_3^2}{x_3 D_{12}}}{\dfrac{x_1}{D_{12}D_{13}} + \dfrac{x_2}{D_{12}D_{23}} + \dfrac{x_3}{D_{23}D_{13}}}$$

For four components or more, COMOL Multiphysics obtains the multicomponent Fick diffusivities numerically through matrix inversion derived from the matrix

properties defined in Ref. 2. The program starts with the multicomponent Maxwell–Stefan diffusivity matrix D_{ik} to compute the multicomponent Fick diffusivity matrix, $\tilde{D}_{ik}$, using the following equation:

$$\tilde{D}_{ij} = N_{ij} - g \tag{3-48}$$

where ij are indices in the matrices $\tilde{D}$ and N, and ranges from 1 to the number of species, Q.

The elements of the matrix N in Equation 3-48 are defined as

$$N_{ij} = (P^{-1})_{ij} \tag{3-49}$$

where P^{-1} is the inverse of a matrix P defined as

$$P_{ij} = \frac{\omega_i \omega_j}{g} - \tilde{C}_{ij}$$

The matrix $\tilde{C}$ in turn is defined as

$$\tilde{C}_{ij} = \begin{cases} \dfrac{x_i x_j}{D_{ij}} & i \neq j \\ -\displaystyle\sum_{k \neq j} \tilde{C}_{ik} & i = j \end{cases}$$

The term g in Equation 3-48 is a scalar value that provides numerical stability and should be of the same order of magnitude as the multicomponent Maxwell–Stefan diffusion coefficients. The physics interface therefore defines q as the sum of the multicomponent Maxwell–Stefan diffusion coefficients:

$$g = \sum_{i=1}^{n-1} \left(\sum_{j=i+1}^{n} D_{ij} \right)$$

Because the multicomponent Fick diffusivity matrix is symmetric, it is sufficient to apply Equation 3-49 to the upper triangle elements of $\tilde{D}$. The remaining elements are obtained by swapping the indices in the matrix.

Multicomponent Diffusion: Mixture-Averaged Approximation

The mixture-averaged diffusion model assumes that the relative mass flux due to molecular diffusion is governed by a Fick's law type approximation.

Assuming that the diffusive flux, relative to the mass averaged velocity, is proportional to the mole fraction gradient, the mass flux is defined as:

$$\mathbf{j}_{\mathrm{md},\,i} = -\rho_i D_i^m \frac{\nabla x_i}{x_i} \tag{3-50}$$

Here ρ_i is the density, and x_i the mole fraction of species i. Using the definition of the species density and mole fraction

$$\rho_i = \rho\omega_i\,,\; x_i = \frac{\omega_i}{M_i}M$$

Equation 3-50 can be expressed in terms of the mass fractions (ω_i) in the manner of

$$\mathbf{j}_{\mathrm{md},\,i} = -\left(\rho D_i^m \nabla\omega_i + \rho\omega_i D_i^m \frac{\nabla M}{M}\right)$$

Using Equation 3-50 together with the Maxwell–Stefan equations, where isobaric and isothermal conditions have been assumed, the following expression for the mixture-averaged diffusion coefficients can be derived (Ref. 3):

$$D_i^m = \frac{1-\omega_i}{\sum_{k\neq i}^{N}\frac{x_k}{D_{ik}}} \tag{3-51}$$

If instead the diffusive flux (relative to the mass averaged velocity) is assumed proportional to the mass fraction gradient, the mass flux is defined as:

$$\mathbf{j}_{\mathrm{md},\,i} = -\rho_i D_i^{m*}\frac{\nabla\omega_i}{\omega_i} = -\rho D_i^{m*}\nabla\omega_i \tag{3-52}$$

For this assumption, using Equation 3-52 together with the Maxwell–Stefan equations, also assuming isobaric and isothermal conditions, the following expression for the mixture-averaged diffusion coefficients can be derived (Ref. 3):

$$\frac{1}{D_i^{m*}} = \sum_{k\neq i}^{N}\frac{x_k}{D_{ik}} + \frac{x_i}{1-\omega_i}\sum_{k\neq i}^{N}\frac{\omega_k}{D_{ik}} \tag{3-53}$$

THE MIXTURE-AVERAGED DIFFUSION COEFFICIENT

When using the mixture-averaged model, the diffusion is proportional to a single diffusion coefficient. The coefficient describes the diffusion of species i relative to the remaining mixture and is referred to as the mixture-averaged diffusion coefficient. The coefficient is explicitly given in terms of the multicomponent Maxwell–Stefan diffusivities D_{ik}. As a consequence, no matrix inversion operation is required as for the Maxwell–Stefan diffusion model (when using four or more species). For low-density gas mixtures, the D_{ik} components can be replaced by the binary diffusivities for the species pairs present.

MIXTURE DIFFUSION CORRECTION

It should be noted that models for the multicomponent diffusivities based on Fick's law are approximations. One drawback of this is that the net diffusive mass flux, the sum of all mass fluxes relative to the mass averaged velocity, is not constrained to zero. To account for this we add a flux, defined by a correction velocity $\mathbf{u}_c$, to enforce a zero net diffusive flux in the manner of:

$$\mathbf{j}_{\mathrm{md},i} = \sum_{i=1}^{N} \rho\omega_i(\mathbf{u}_{\mathrm{d},i} + \mathbf{u}_c) = 0 \tag{3-54}$$

Hence the correction velocity is:

$$\mathbf{u}_c = -\sum_{i=1}^{N} \omega_i \mathbf{u}_{\mathrm{d},i} \tag{3-55}$$

Here $\mathbf{u}_{\mathrm{d},i}$ is the diffusion velocity resulting from the flux assumption in Equation 3-50 or Equation 3-52. Note that the correction velocity is a constant correction (same for all species), but varies in space.

Using the correction velocity together with Equation 3-50, the resulting diffusive flux is

$$\mathbf{j}_{\mathrm{md},i} = -\rho D_i^m \nabla\omega_i - \rho\omega_i D_i^m \frac{\nabla M}{M} + \rho\omega_i \sum_{i=1}^{N} \frac{M_i}{M} D_i^m \nabla x_i \tag{3-56}$$

If instead Equation 3-52 is used the resulting diffusive flux is

$$\mathbf{j}_{\mathrm{md},i} = -\rho D_i^{m*} \nabla\omega_i + \rho\omega_i \sum_{i=1}^{N} D_i^{m*} \nabla\omega_i \tag{3-57}$$

ADDITIONAL TRANSPORT MECHANISMS

Apart from molecular diffusion, transport due to thermal diffusion and migration of charged species in an electric field can be accounted for by adding the following terms to the diffusive flux:

$$\mathbf{j}_i = \nabla \cdot \left(D_i^T \frac{\nabla T}{T} + \rho \omega_i z_i u_{m,i} F \nabla \phi \right)$$

where

- D_i^T (SI unit: kg/(m·s)) is the thermal diffusion coefficient
- z_i (dimensionless) is the charge number
- $u_{m,i}$ the mobility of the i^{th} species, and
- ϕ (SI unit: V) is the electric potential.

Multispecies Diffusion: Fick's Law Approximation

Using a ***Fick's law approximation***, the relative mass flux due to molecular diffusion is governed by

$$\mathbf{j}_{\text{md},i} = -\rho_i D_{i,kl}^F \frac{\nabla x_i}{x_i} \tag{3-58}$$

when assuming that the diffusive flux is proportional to the mole fraction gradient. If instead assuming that it is proportional to the mass fraction it becomes

$$\mathbf{j}_{\text{md},i} = -\rho D_{i,kl}^F \nabla \omega_i \tag{3-59}$$

In the equations above $D_{i,kl}^F$ represents a general diffusion matrix (SI unit: m^2/s) describing the diffusion of species i into the mixture. This form makes it possible to use any diffusion coefficient, matrix, or empirical model based on Fick's law. For example, in situations when the mass transport is not dominated by diffusion, an alternative is to use the diffusion coefficients at infinite dilution,

$$D_{i,kk}^F = D_i^0$$

These coefficients are typically more readily available compared to the binary diffusion diffusivities, especially for liquid mixtures.

The mixture diffusion correction described above for the mixture-averaged diffusion can also be applied in this case. Correspondingly, the resulting diffusive flux is

$$\mathbf{j}_{\mathrm{md},i} = -\rho D_{i,kl}^{F}\nabla\omega_i - \rho\omega_i D_{i,kl}^{F}\frac{\nabla M}{M} + \rho\omega_i\sum_{i=1}^{N}\frac{M_i}{M}D_{i,kl}^{F}\nabla x_i \qquad (3\text{-}60)$$

when using Equation 3-58 and

$$\mathbf{j}_{\mathrm{md},i} = -\rho D_{i,kl}^{F}\nabla\omega_i + \rho\omega_i\sum_{i=1}^{N}D_{i,kl}^{F}\nabla\omega_i \qquad (3\text{-}61)$$

when instead using Equation 3-59.

When using the Fick's Law approximation, Additional Transport Mechanisms can be accounted for in the same manner as described above for the mixture-averaged approximation.

Multicomponent Thermal Diffusion

Mass diffusion in multicomponent mixtures due to temperature gradients is referred to as the *Soret effect*. This occurs in mixtures with high temperature gradients and large variations in molecular weight (or size) of the species. Typically species with high molecular weight accumulate in lower temperature regions while the diffusion due to the Soret effect transports species with low molecular weight to higher temperature regions. In COMSOL Multiphysics, thermal diffusion is included by prescribing the thermal diffusion coefficients D_i^T. In a multicomponent mixture, the sum of the thermal diffusion coefficients is zero:

$$\sum_{i=1}^{Q} D_i^T = 0$$

Reactive Pellet Bed

The Reactive Pellet Bed, available in the Transport of Concentrated Species interface, is a domain feature that can simulate porous regions filled with reactive catalyst pellets, as in packed bed reactors. The pellets are simulated with the Extra Dimension technology provided by the COMSOL software: A base geometry (1D, 2D, or 3D)

domain represents the bed volume. The extra dimension is the added radial microscale dimension inside each pellet.

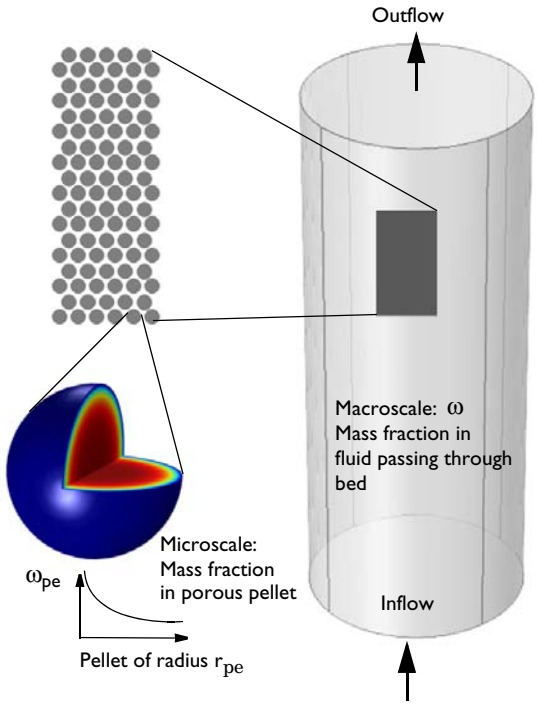


Figure 3-5: Schematic showing the macroscale (bed volume) and the microscale (pellet).

The equations of mass and momentum transfers inside the pellets are solved on an extra dimension attached to the 1D, 2D, or 3D physics interfaces, including axisymmetric cases.

The equations inside the spherical pellet are solved as a spherical transport equations on a nondimensional radial coordinate on the domain 0-1. A given pellet size or a discrete distribution of sizes can be used.

The model equations assume spherical particles (pellets) of a radius r_{pe}. Modeling assumptions for cylinders, flakes, and user-defined shapes can also be used. Consider the microscale mass fraction $\omega_{pe,i}$ inside an individual porous pellet or pellets, and the macro mass fraction ω_i in the packed bed volume.

The pellet radius input can be:

- One uniform pellet radius, which can be space dependent $f(x, y, z)$.
- Binary, ternary, and so on, mix up to 5 radii. The user inputs a table with the mix of sizes (1 mm, 2 mm, for example), and volume fraction of each. Different chemical reactions per pellet size can be specified.

The model equations in the macroscale (base geometry) for the species mass fraction i and velocity (Darcy's Law) are, for example:

$$\varepsilon_b \rho \frac{\partial \omega_i}{\partial t} + \nabla \cdot (\mathbf{J}_i) + \rho \mathbf{u} \cdot \Delta \omega_i = R_i \tag{3-62}$$

$$\frac{\partial}{\partial t}(\varepsilon_b \rho) + \nabla \cdot (\rho \mathbf{u}) = Q_m \tag{3-63}$$

- ε_b is the bed porosity.
- The dependent variable ω_i for each chemical species i represents the interstitial mass fraction, that is, based on unit volume of fluid flowing between the pellets.
- $\mathbf{J}_i$ is the mass flux for species i.
- R_i is the species reaction rate (kg/(m^3·s)) in the bed. This corresponds to reactions occurring in the pore space outside of the pellets. Note, that R_i is the reaction rate per unit volume of bed.
- Q_m is the mass source (kg/(m^3·s)).

Looking inside a pellet: Assuming no concentration variations in the space-angle (θ, φ) direction, but only in the radial (r) direction of the spherical pellet allows a spherically symmetric reaction-diffusion transport equation inside the pellet. If r_{dim} (SI unit: m) is the spatial radial coordinate in the pellet, and r_{pe} is the pellet radius, the nondimensional coordinate $r = r_{dim}/r_{pe}$ can be defined. The modeling domain on r goes from 0 to 1.

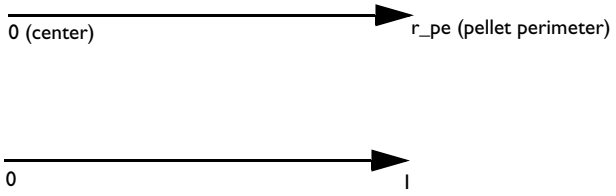


Figure 3-6: Modeling domain in a pellet for dimensional (top) and nondimensional (bottom) coordinates.

A shell mass balance across a spherical shell at radius r_{dim} (SI unit: m), and a subsequent variable substitution $r = r_{\text{dim}}/r_{\text{pe}}$ gives the following mass transport equation on the pellet domain $0 < r < 1$, Equation 3-21 becomes

$$4\pi N\left\{r^2 {r_{\text{pe}}}^2 \varepsilon_{\text{pe}} \frac{\partial}{\partial t}(\omega_{\text{pe},i}) + \nabla \cdot (r^2 \mathbf{J}_{pe,i}) + r^2 r_{\text{pe}} (\rho \mathbf{u})_{\text{pe}} \cdot (\nabla \omega_{\text{pe},i})\right\} = 4\pi N\left\{r^2 {r_{\text{pe}}}^2 R_{\text{pe},i}\right\} \tag{3-64}$$

- N is the number of pellets per unit volume of bed, $N = \dfrac{(1-\varepsilon_{\text{b}})}{V_{\text{pe}}}$, V_{pe} is the pellet volume.
- ε_{pe} is the pellet (microscale) porosity.
- As in Equation 3-22, $\omega_{\text{pe,i}}$ is the interstitial (physical) species mass fraction of fluid volume element inside the pore channel in the pellet.
- $\mathbf{J}_{\text{pe,i}}$ is the mass flux for species *i* inside pellet. It is similar to the mass flux in Transport of Concentrated Species.
- $\mathbf{u}_{\text{pe}}$ is the velocity of mass bulk in the pellet.
- $R_{\text{pe,i}}$ is the pellet reaction rate for species *i*. This corresponds to reactions taking place inside the pellets. Note that the user input of $R_{\text{pe,i}}$ is per unit volume of pellet.

The velocity u is calculated from pressure gradient,

$$\mathbf{u}_{\mathrm{pe}} = -\frac{\kappa_{\mathrm{pe}}}{\mu_{\mathrm{pe}}}\nabla p_{\mathrm{pe}}$$

- κ_{pe} is the permeability inside pellet.
- μ_{pe} is the dynamic viscosity inside pellet.

The equation for pressure p_{pe} (base on Equation 3-63) on the pellet domain, $0 < r < 1$, is

$$4\pi N\left\{r^2 {r_{\mathrm{pe}}}^2 \varepsilon_{\mathrm{pe}} \frac{\partial p_{\mathrm{pe}}}{\partial t} + r^2 \nabla \cdot (r^2(\rho \mathbf{u})_{\mathrm{pe}}) = r^2 {r_{\mathrm{pe}}}^2 Q_{\mathrm{m}}\right\} \tag{3-65}$$

The mass flux $\mathbf{J}_{\mathrm{i}}$ in Equation 3-22, with diffusion model being Mixture-averaged, is

$$J_{\mathrm{pe},i} = -\left(\rho_{\mathrm{pe}} {D_i}^m \nabla \omega_{\mathrm{pe},i} + \rho_{\mathrm{pe}} \omega_{\mathrm{pe},i} {D_i}^m \frac{\nabla M_{\mathrm{pe,n}}}{M_{\mathrm{pe,n}}} + {D_{\mathrm{e},i}}^T \frac{\nabla T_{\mathrm{pe}}}{T_{\mathrm{pe}}}\right) \tag{3-66}$$

where ${D_{\mathrm{e,i}}}^{\mathrm{T}}$ is the effective thermal diffusion coefficient, and ${D_i}^m$ is

$${D_i}^m = \frac{1 - \omega_{\mathrm{pe},i}}{\sum_{k \neq i} \frac{x_{\mathrm{pe},k}}{D_{\mathrm{e},ik}}}$$

If the diffusion model is Maxwell-Stefan, the equation for mass flux $\mathbf{J}_{\mathrm{i}}$ is

$$J_{\mathrm{pe},i} = -\left(\rho_{\mathrm{pe}} \omega_{\mathrm{pe},i} \sum_k \overline{D}_{\mathrm{e},ik} \mathbf{d}_k + {D_{\mathrm{e},i}}^T \frac{\nabla T_{\mathrm{pe}}}{T_{\mathrm{pe}}}\right) \tag{3-67}$$

where $\mathbf{d}_k$ is

$$\mathbf{d}_k = \nabla x_{\mathrm{pe},k} + \frac{1}{p_{\mathrm{pe}}}[(x_{\mathrm{pe},k} - \omega_{\mathrm{pe},k})\nabla p_{\mathrm{pe}}]$$

where $D_{\mathrm{e,ik}}$ is the effective binary diffusion coefficient. It depends on the porosity $\varepsilon_{\mathrm{pe}}$, tortuosity τ, and binary diffusion coefficient D_{ik}

$$D_{e,ik} = \frac{\varepsilon_{\mathrm{pe}} D_{ik}}{\tau}$$

The available models for the porous media tortuosity are the one by Millington and Quirk (Ref. 4),

$$\tau = \varepsilon_{\mathrm{pe}}^{-1/3} \Rightarrow D_{\mathrm{e},ik} = \varepsilon_{\mathrm{pe}}^{4/3} D_{ik}\,, \tag{3-68}$$

the Bruggeman model,

$$\tau = \varepsilon_{\mathrm{pe}}^{-1/2} \Rightarrow D_{\mathrm{e},ik} = \varepsilon_{\mathrm{pe}}^{3/2} D_{ik} \tag{3-69}$$

and the Tortuosity model, where the tortuosity expression is entered as user defined input.

These are readily used for both gaseous and liquid fluids along with various types of pellet shapes.

Equation 3-22 and Equation 3-65 can be solved for two types of boundary conditions at the interface between the pellet surface and the fluid in this feature.

- **Mass fraction constraint:** assuming that all resistance to mass transfer to/from the pellet is within the pellet and no resistance to pellet-fluid mass transfer is on the bulk fluid side. The mass fraction and pressure in the fluid will thus be equal to that in the pellet pore just at the pellet surface: $\omega_{\mathrm{pe},i} = \omega_i$ and $p_{\mathrm{pe}} = p_A$. These constraints also automatically ensure flux continuity between the internal pellet domain and the free fluid domain through so-called reaction forces in the finite element formulation.
- **Film resistance (mass flux):** The flux of mass across the pellet-fluid interface into the pellet is possibly rate determined on the bulk fluid side by film resistance. The resistance is expressed in terms of a film mass transfer coefficient, h_{Di}, such that:

$$N_{i,\mathrm{inward}} = h_{\mathrm{D},i}(c_i - c_{\mathrm{pe},i})M_i\,, \tag{3-70}$$

  where $N_{i,\mathrm{inward}}$ is the mass flux from the free fluid into a pellet and has the unit kg/(m^2·s), M_i is the molar mass.

With the film resistance formulation above, the equation for mass transfer (Equation 3-22) needs to be amended for flux continuity so that

$$4\pi N\left\{r^2 r_{\mathrm{pe}}{}^2 \varepsilon_{\mathrm{pe}} \frac{\partial}{\partial t}(\omega_{\mathrm{pe},i}) + \nabla\cdot(r^2 J_{\mathrm{pe},i}) + r^2 r_{\mathrm{pe}}(\rho\mathbf{u})_{\mathrm{pe}}\cdot(\nabla\omega_{\mathrm{pe},i})\right\} = 4\pi N\left\{r^2 r_{\mathrm{pe}}{}^2 (R_{\mathrm{pe},i} - N_{i,\mathrm{inward}} S_{\mathrm{b}})\right\} \tag{3-71}$$

where S_b (SI unit: m^2/m^3) is the specific surface area exposed to the free fluid of the packed bed (not including the inside of the pores).

For the case of randomly packed spherical pellets, the specific surface area exposed to the free fluid is (Ref. 5):

$$S_b = \frac{3}{r_{pe}}(1 - \varepsilon_b) \tag{3-72}$$

The total mass source Q_{mass} is

$$Q_{mass} = \sum_i N_{i,\,inward} S_b$$

The equation for pressure (Equation 3-65) becomes

$$4\pi N\left\{r^2 r_{pe}{}^2 \varepsilon_{pe} \frac{\partial p_{pe}}{\partial t} + r^2 \nabla \cdot (r^2 (\rho \mathbf{u})_{pe}) = r^2 r_{pe}{}^2 (Q_m - Q_{mass})\right\} \tag{3-73}$$

The mass transfer coefficient in Equation 3-27 can be computed from the fluid properties and flow characteristics within the porous media. For this, the Sherwood, Sh, number defined as the ratio between the convective mass transfer coefficient and the diffusive mass transfer coefficient is often used:

$$\mathrm{Sh} = \frac{hL}{D}$$

where L is a characteristic length (for spheres, typically the radius), and D is the diffusion coefficient in the fluid. From the Sherwood number definition, the mass transfer coefficient can be computed.

Three commonly used empirical expressions for the calculation of the Sherwood number are the Frössling relation (Ref. 6):

$$\mathrm{Sh} = 2 + 0.552 \mathrm{Re}^{1/2} \mathrm{Sc}^{1/3}\,, \tag{3-74}$$

which was measured on pellets in the size region 1 mm, the Rosner relation (Ref. 7)

$$\mathrm{Sh} = \mathrm{Sc}^{0.4}(0.4\mathrm{Re}^{1/2} + 0.2\mathrm{Re}^{2/3})\,, \tag{3-75}$$

and the Garner and Keey relation (Ref. 6)

$$\mathrm{Sh} = 0.94 \mathrm{Re}^{1/2} \mathrm{Sc}^{1/3}\,, \tag{3-76}$$

which was measured for Re numbers greater than 250.

All three depend on the Reynolds, Re, and Schmidt, Sc, numbers. The first describing the fluid flow regime (laminar versus turbulent) and the second, the ratio between the viscous diffusion rate and the molecular (mass) diffusion rate. In the expressions, properties such as velocity, u, dynamic viscosity, μ, and density, ρ, of the fluid are included.

$$\mathrm{Re} = \frac{\rho u L}{\mu}$$

$$\mathrm{Sc} = \frac{\mu}{\rho D}$$

NONSPHERICAL PARTICLES

For nonspherical pellets (of any shape), the relations above can be applied approximately by reinterpreting the pellet radius r_{pe} as

$$r_{pe} = 3\frac{V_{pe}}{A_{pe}} \tag{3-77}$$

(Ref. 8), where A_{pe} is the external surface of a single pellet of any shape. Since the specific surface S_{pe} (SI unit: m^2/m^3) of one pellet is defined as

$$S_{pe} = \frac{A_{pe}}{V_{pe}}$$

it follows by insertion of Equation 3-35 that

$$S_{pe} = \frac{3}{r_{pe}}.$$

For a packed bed of which the packing has a porosity ε_b, the specific surface of the bed will be

$$S_b = S_{pe}(1-\varepsilon_b) = \frac{A_{pe}}{V_{pe}}(1-\varepsilon_b)$$

or

$$S_b = \frac{3}{r_{pe}}(1-\varepsilon_b) \tag{3-78}$$

for any pellet shape. Now r_{pe} and S_b can be calculated for any shape and inserted in equations Equation 3-22, Equation 3-65, Equation 3-28 and Equation 3-73. Some common specific shapes have automatic support:

Cylinders

For cylindrical shapes, applying Equation 3-35 gives

$$r_{pe} = 3\frac{V_{pe}}{A_{pe}} = 3\frac{\pi r_{cyl}^2 L_{cyl}}{2\pi r_{cyl} L_{cyl} + 2\pi r_{cyl}^2} = \frac{1}{\frac{2}{3r_{cyl}} + \frac{2}{3L_{cyl}}}. \quad (3\text{-}79)$$

It is common practice to assume that the top and bottom surface of cylindrical pellets have negligible effect on the mass transfer to and from the internals of the pellet, or, $r_{cyl} \ll L_{cyl}$. Equation 3-37 then simplifies to

$$r_{pe} = \frac{3}{2} r_{cyl}$$

and Equation 3-36 to

$$S_b = \frac{2}{r_{cyl}}(1 - \varepsilon_b)$$

Flakes

The derivation for a disc-shaped catalyst pellet is exactly the same as for cylindrical pellets, except that the assumption is reversed about the end surfaces and the envelope surface: $r_{flake} \gg w_{flake}$, where w_{flake} is the thickness of the disc. This gives

$$r_{pe} = \frac{3}{2} w_{flake}$$

and

$$S_b = \frac{2}{w_{flake}}(1 - \varepsilon_b).$$

HEAT SOURCE

The heat source of endothermic or exothermic reactions inside the pellet needs to be accounted for in the heat transfer on the bulk level if the heat balance is not solved within the pellet. In this case, thermal equilibrium is assumed in each pellet. To account for the heat evolution in the bulk, the source is averaged across the pellet:

$$Q_{\text{bed}} = \frac{\int Q_{\text{pe}} dV}{V_{\text{pe}}}(1-\varepsilon_{\text{b}}) \ (\text{W/m}^3)$$

If there are multiple pellet sizes i in the bed the heat source computed by summing over all sizes:

$$Q_{\text{bed}} = \sum_i (Q_{\text{bed},\,i} \cdot \theta_{\text{v},i})$$

Here $\theta_{\text{v},i}$ is the volume fraction of pellet i in the pellet mix.

Regularization of Reaction Rate Expression

The flexibility of COMSOL means that a reaction can result in nearly any reaction rate contribution R_i^{c} to a mass fraction ω_i. But a reactant, ω_r, can physically only be consumed if $\omega_r > 0$ and a product, ω_k, can only be formed if $\omega_k < 1$. The Reaction feature in Transport of Concentrated Species Interface contains a way to regularize make the rate expression contributions comply to these restrictions.

When selected the "core", or unregularized reaction rate contribution, R_i^{c}, to a mass fraction ω_i is replaced by

$$R_i = \frac{1}{2}\frac{R_i^{\text{c}} - \left|R_i^{\text{c}}\right|}{\max(\omega_i, \omega_i^{\text{dl}})}\max(\omega_i, 0) + \frac{1}{2}\frac{R_i^{\text{c}} + \left|R_i^{\text{c}}\right|}{\max(1-\omega_i, \omega_i^{\text{dl}})}\max(1-\omega_i, 0) \qquad (3\text{-}80)$$

The first term on the right hand side of Equation 3-80 is active if $R_i^{\text{c}} < 0$, that is if ω_i is a reactant. The reaction rate contribution, R_i, is equal to the "core" reaction rate, R_i^{c}, as long as $\omega_i > \omega_i^{\text{dl}}$. As ω_i approaches zero, the regularization damps out negative R_i^{c} and for $\omega_i < 0$, R_i for reactant ω_i is equal to zero.

The second term on the right hand side of Equation 3-80 is active if $R_i^{\text{c}} > 0$, that is if ω_i is a product. The reaction rate contribution, R_i, is equal to the "core" reaction rate, R_i^{c}, as long as $\omega_i < 1–\omega_i^{\text{dl}}$. As ω_i approaches one, the regularization damps out positive R_i^{c} and for $\omega_i > 1$, R_i for product ω_i is equal to zero.

The damping limits, ω_i^{dl}, should be in an order of magnitude that can be considered numerical noise for species i. The damping limits are per default set to $1e^{-6}$, which is appropriate for most applications. It can be advantageous to lower some limits when

working with for example catalytic trace species and the limits can sometimes be raised to gain additional robustness.

References for the Transport of Concentrated Species Interface

1. C.F. Curtiss and R.B. Bird, "Multicomponent Diffusion", *Ind. Chem. Res.*, vol. 38 pp. 2515–2522, 1999.

2. R.B. Bird, W.E. Stewart, and E.N. Lightfoot, *Transport Phenomena*, 2nd ed., John Wiley & Sons, 2005.

3. R.J. Kee, M.E. Coltrin, and P. Glarborg, *Chemically Reacting Flow*, John Wiley & Sons, 2003.

4. R.J. Millington and J.M. Quirk, "Permeability of Porous Solids", *Trans. Faraday Soc.*, vol. 57, pp. 1200–1207, 1961.

5. J.M. Coulson and J.F. Richardson, *Chemical Engineering, vol. 2*, 4th ed., Pergamon Press, Oxford, U.K., 1991.

6. J.M. Coulson and J.F. Richardson, *Chemical Engineering, vol. 1*, 4th ed., Pergamon Press, Oxford, U.K., 1991.

7. D.E Rosner, *Transport Processes in Chemically Reacting Flow Systems*, ISBN-13: 978-1483130262, Butterworth-Heinemann, 1986.

8. R.B. Bird, W.E. Stewart, and E.N. Lightfoot, *Transport Phenomena*, 2nd ed., John Wiley & Sons, Inc., 2007.

Theory for the Electrophoretic Transport Interface

The Electrophoretic Transport Interface models transport of charged and uncharged species, and in addition sets up a charge balance equation for the electrolyte potential.

The species concentrations are denoted, c_i (SI unit: mol/m^3), and the potential, ϕ_l (SI unit: V).

The species are transported by diffusion, migration, and (optionally) convection according the Nernst-Planck set of equations. The total flux of species i is denoted $\mathbf{N}_i$ (SI unit: mol/(m^2·s)) according to

$$\mathbf{N}_i = -D_i\nabla c_i - z_i u_{m,i} F c_i \nabla\phi_l + \mathbf{u}c_i = \mathbf{J}_i + \mathbf{u}c_i \tag{3-81}$$

where D_i (SI unit: m^2/s) is the diffusion coefficient, z_i (1) the corresponding charge, $u_{m,i}$ (SI unit: s·mol/kg) the mobility and $\mathbf{u}$ (SI unit: m/s) the velocity vector. $\mathbf{J}_i$ denotes the molar flux relative to the convective transport (SI unit: mol/(m^2·s)). For a detailed description of the theory of these equations and the different boundary conditions, see Theory for the Transport of Diluted Species Interface.

CHARGE BALANCE EQUATION

The current vector, $\mathbf{i}_l$ (A/m^2), is defined as

$$\mathbf{i}_l = \sum_i z_i \mathbf{N}_i \tag{3-82}$$

where the summation is made over all species in the electrolyte.

The governing equation for the electrolyte potential is

$$\nabla\cdot\mathbf{i}_l = Q_l \tag{3-83}$$

where Q_l (SI unit: A/m^3) is the electrolyte current source stemming from, for example, porous electrode reactions. For non-porous electrode domains this source term is usually zero.

PROTON AND HYDROXIDE CONCENTRATIONS AND ELECTRONEUTRALITY

Assuming the total number of species to be N+2, the assumption of electroneutrality is

$$\sum_{i=1}^{N+2} z_i c_i = 0 \tag{3-84}$$

In water-based systems the species H+ and OH- are always present. The auto ionization reaction for water is

$$H_2O \leftrightarrow H^+ + OH^- \tag{3-85}$$

This reaction is fast, following the equilibrium relation

$$c_{H^+} c_{OH^-} = K_w \times 1 \text{ mol}^2\text{dm}^{-6} \tag{3-86}$$

where $K_w \approx 10^{-14}$.

Now, the electroneutrality condition, including the two additional species H+ and OH-, reads

$$c_{H^+} - c_{OH^-} + \sum_{i=1}^{N} z_i c_i = 0 \tag{3-87}$$

Combining these two equations results in the following algebraic expressions for the concentrations of H+ and OH-.

$$c_{H^+} = -\frac{\Sigma}{2} + \sqrt{\frac{\Sigma^2}{4} + K_w \times 1 \text{ mol}^2\text{dm}^{-6}} \tag{3-88}$$

and

$$c_{OH^-} = \frac{\Sigma}{2} + \sqrt{\frac{\Sigma^2}{4} + K_w \times 1 \text{ mol}^2\text{dm}^{-6}} \tag{3-89}$$

where

$$\Sigma = \sum_{i=1}^{N} z_i c_i \tag{3-90}$$

MASS BALANCE EQUATIONS FOR DISSOCIATION SPECIES

Assume a set of species Si describing k dissociation steps from

$$S_k^{z_0+k} \leftrightarrow S_{k-1}^{z_0+k-1} + H^+ \qquad K_{a,1} = \frac{[H^+][S_{k-1}^{z_0+k-1}]}{[S_k^{z_0+k}]} \tag{3-91}$$

to

$$S_k^{z_0+1} \leftrightarrow S_0^{z_0} + H^+ \qquad K_{a,k} = \frac{[H^+][S_0^{z_0}]}{[S_1^{z_0+1}]} \tag{3-92}$$

where z_0 is the charge (valence) of species S_0 (which has no dissociable protons) and $K_{a,j}$ is the acid (equilibrium) constant of the j*th* dissociation reaction. The brackets [ ] here represents the species activity. The charge of each species is always deductible from the index i according to z_{0+i} and will be dropped from now on.

If the proton activity is known, any species S_m may be expressed using any other species S_l according to

$$[S_m] = \frac{[H]^{m-l}[S_l]}{\prod_{j=k-m+1}^{k-l} K_{a,j}} \tag{3-93}$$

if $m>l$ and

$$[S_m] = [H]^{m-l}[S_l] \prod_{j=k-l+1}^{k-m} K_{a,j} \tag{3-94}$$

if $l>m$.

Setting $m=i$ and denoting the flux of species i by $\mathbf{N}_i$ using equation Equation 3-81, the mass balance equation for the concentration c_i of each subspecies i in the dissociation chain is

$$\frac{\delta c_i}{\delta t} + \nabla \cdot \mathbf{N}_i = R_{\text{eq},i,k-i} - R_{\text{eq},i,k-i+1} + R_i \tag{3-95}$$

where $R_{\text{eq},i,j}$ is the reaction source stemming from the jth dissociation step (with $R_{\text{eq},i,k+1}=0$), and R_i any additional reaction sources.

The reaction source contributions from the dissociation steps are generally not known, but may be canceled by taking the sum of all mass balance equations, resulting in

$$\sum_{i=0}^{k}\left(\frac{\delta c_i}{\delta t}+\nabla\cdot\mathbf{N}_i\right)=\sum_{i=0}^{k}R_i \tag{3-96}$$

AVERAGE IONIZATION FORMULATION FOR LARGE MOLECULES

Large protein molecules are typically subject to a large number of dissociation steps.

As an alternative way to a long chain of dissociation steps for describing protein transport, one can instead formulate the protein transport based on the average number of protons $\bar{\nu}$ (1) removed from the molecule. $\bar{\nu}$ is typically provided as a function of pH, based on experimental data. The average charge of the species then is $\bar{z}=z_0-\bar{\nu}$, so that the flux of the species is written as:

$$\mathbf{N}_i=-D\nabla c_i-\bar{z}u_m F c_i\nabla\phi_l+\mathbf{u}c_i \tag{3-97}$$

and similarly the addition to the charge neutrality condition is $\bar{z}c_i$.

When considering the contribution to the current and the charge balance equation one needs to take into account that the squared average charge, $\bar{z}^2=(z_0-\bar{\nu})^2$, is not equal to the "average squared charge", $\overline{z^2}=z_0^2+2z_0\bar{\nu}+\overline{\nu^2}=\bar{z}^2-\bar{\nu}^2+\overline{\nu^2}$ (Ref. 1).

The addition to the current density vector is

$$\mathbf{i}_l=\ldots-F(\bar{z}D_i\nabla c_i+\overline{z^2}u_m c_i\nabla\phi_l) \tag{3-98}$$

The average number of protons removed from the proton typically depends on the pH. If the average number of removed protons depend only on the pH, the averaged squared number of protons removed can be written as

$$\overline{\nu^2}=-c_{\mathrm{H^+}}\frac{d}{dc_{\mathrm{H^+}}}\bar{\nu}+\bar{\nu}^2 \tag{3-99}$$

And from this one can derive the average squared charge according to

$$\overline{z^2}=-c_{\mathrm{H^+}}\frac{d}{dc_{H^+}}\bar{\nu}+\bar{z}^2=-c_{\mathrm{H^+}}\frac{d}{dc_{\mathrm{H^+}}}\bar{z}+\bar{z}^2 \tag{3-100}$$

DIFFUSIVITY-MOBILITY RELATIONS

The Stokes radius r of a molecule is related to the diffusivity according to

$$r=\frac{kT}{6\pi\mu D} \tag{3-101}$$

where is the μ (SI unit: Pa·s) is the dynamic viscosity and k the Boltzmann constant.

For small molecules, one frequently uses the Nernst-Einstein relation between the diffusivity and the mobility

$$u_m = \frac{D}{RT} \tag{3-102}$$

For larger molecules, such as proteins, the mobility may instead be calculated based on the Debye-Hückel-Henry expression (Ref. 2) according to

$$u_m = \frac{ef(\kappa r)}{6\pi\mu F(1+\kappa r)} = \frac{Df(\kappa r)}{RT(1+\kappa r)} \tag{3-103}$$

where κ (1/m) is the Debye parameter, which depends on the ionic strength of the solution, is defined for ideal solutions as

$$\kappa^2 = \frac{2e^2 N_A}{\varepsilon\varepsilon_0 kT}\sum_{i=1}^{N} z_i^2 c_i \tag{3-104}$$

where ε is the dielectric constant of the fluid and ε_0 the permittivity of free space. ($\overline{z^2}$ should be used if available in the formula above when calculating the ionic strength).

The function f above is based on a sigmoidal function so that it ranges from 1 for $\kappa r = 0$ to 1.5 for $\kappa r = \infty$. Note that the Debye-Hückel-Henry expression approaches the Nernst-Einstein mobility as $r \to 0$.

For larger molecules (macro ions), where the distance between the charges is large compared to 1/κ, the Linderstrøm-Lang approximation postulates a smaller contribution of to the ionic strength so that the z-valent ion behaves as a monovalent ion with a z-fold concentration. For an assemble of N-M smaller molecules and M macro ions, the Debye parameter then is defined as

$$\kappa^2 = \frac{2e^2 N_A}{\varepsilon\varepsilon_0 kT}\left(\sum_{i=1}^{N-M} z_i^2 c_i + \sum_{i=N-M+1}^{N} \mathrm{abs}(z_i) c_i\right) \tag{3-105}$$

REFERENCES

1 *The Dynamics of Electrophoresis*, Mosher, Saville and Thormann, VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1992.

2 *Computer Simulation and Experimental Validation of the Electrophoretic Behavior of Proteins. 2. Model Improvement and Application to Isotachophoresis,* Mosher, Gebauer, Caslavska, and Thormann. *Analytical Chemistry*, Vol. 64, pp. 2991–2997, 1992.

Theory for the Surface Reactions Interface

The Surface Reactions Interface solves for an arbitrary number of surface concentrations, $c_{s,i}$ (SI unit: mol/m^2), referring to species adsorbed on a reactive surface, and an arbitrary number of bulk concentrations $c_{b,k}$ (SI unit: mol/m^3), referring to the species in the solid material that constitutes the bulk of the reactive surface.

In this section:

- Governing Equations for the Surface Concentrations
- Governing Equations for the Bulk Concentrations
- ODE Formulations for Surface Concentrations
- Surface Reaction Equations on Deforming Geometries
- Reference for the Surface Reactions Interface

Governing Equations for the Surface Concentrations

Transport of adsorbed species occurs in the tangential direction along the surface. The Surface Reactions interface models the tangential flux in the surface dimension, the *surface molar flux*, $\mathbf{N}_{t,i}$ (SI unit: mol/(m·s)) (the subscript t refers to the tangential direction), as governed by diffusion according to Fick's law:

$$\mathbf{N}_{t,i} = -D_{s,i}\nabla_t c_{s,i}$$

where $D_{s,i}$ (SI unit: m^2/s) is the surface diffusion coefficient for species i.

The governing equation for the surface concentrations is written as:

$$\frac{\partial c_{s,i}}{\partial t} = -\nabla_t \cdot \mathbf{N}_{t,i} + R_{s,i} \tag{3-106}$$

where $R_{s,i}$ (SI unit: mol/(m^2·s)) is the sum of all sources due to surface reactions and adsorption/desorption phenomena.

Of frequent interest for surface reaction kinetics are the fractional surface coverages, θ_i (dimensionless), of the species (with index i).

Writing the density of sites of the surface as Γ_s (SI unit: mol/m^2) and the site occupancy number for each species as σ_i (dimensionless), the surface coverages can be calculated from:

$$\theta_i = \frac{\sigma_i c_{s,i}}{\Gamma_s}$$

(The site occupancy number accounts for the situation when a large species covers more than one site on the surface.)

For the case of monolayer adsorption, the sum of all fractional coverages of free and adsorbed sites is unity, and hence the fraction of free sites on the surface, θ_*, can be calculated from:

$$\theta_* = 1 - \sum_i \theta_i$$

Governing Equations for the Bulk Concentrations

BULK SPECIES RATES AND GROWTH VELOCITY

The reaction rate for a bulk species of index k, being added to the bulk due to surface reactions is defined as $R_{b,k}$ (SI unit: mol/(s·m^2)).

The reaction rate in mass basis, $r_{b,k}$ (SI unit: kg/(s·m^2)) for species k, is given by:

$$r_k = M_k R_{b,k}$$

with M_k (SI unit: kg/mol) being the molar mass of the species.

Based on this, the species contribution to the bulk growth velocity, v_k (SI unit: m/s), is given by:

$$v_{b,k} = \frac{r_{b,k}}{\rho_k}$$

where ρ_k is the species density (SI unit: kg/m^3).

TOTAL RATES AND VELOCITY

To get the corresponding total values, a summation for all bulk species is made according to:

$$R_{b,\,\text{tot}} = \sum_k R_{b,\,k}$$

$$r_{b,\,\text{tot}} = \sum_k r_{b,\,k}$$

$$v_{b,\,\text{tot}} = \sum_k v_{b,\,k}$$

FRACTIONAL RATES AND VELOCITY

The fractional deposition rates are calculated by:

$$R_{b,\,\text{frac},\,k} = \frac{R_{b,\,k}}{R_{b,\,\text{tot}}}$$

$$r_{b,\,\text{frac},\,k} = \frac{r_{b,\,k}}{r_{b,\,\text{tot}}}$$

$$v_{b,\,\text{frac},\,k} = \frac{v_{b,\,k}}{v_{b,\,\text{tot}}}$$

The fractional deposition rates can be used as measures of the local fractional composition in a deposited layer at a certain thickness or time.

ACCUMULATED BULK QUANTITIES

By solving for the bulk species concentrations for each time step, the accumulated mass and thickness changes of the bulk material can be calculated.

The bulk concentration, $c_{b,k}$ (SI unit: mol/m^2), for species k is governed by the equation:

$$\frac{\partial c_{b,\,k}}{\partial t} = R_{b,\,k} \tag{3-107}$$

The bulk concentration in mass basis, $m_{b,k}$ (SI unit: kg/m^2) for a species k, can be derived from:

$$m_{b,\,k} = M_k c_{b,\,k}$$

leading to the bulk thickness $s_{b,k}$ (SI unit: m) of species k according to:

$$s_{b,\,k} = \frac{m_{b,\,k}}{\rho_k}$$

TOTAL BULK QUANTITIES

The total bulk concentration is calculated according to:

$$c_{b,\,\text{tot}} = \sum_k c_{b,\,k}$$

The deposited total mass, $m_{b,\text{tot}}$ (SI unit: kg/m^2) is

$$m_{b,\,\text{tot}} = \sum_k m_{b,\,k}$$

and the total bulk thickness, s_{tot} (SI unit: m) is

$$s_{b,\,\text{tot}} = \sum_k s_k$$

FRACTIONAL QUANTITIES

The fractional bulk concentration, bulk mass, and thickness (all dimensionless) are calculated according to:

$$c_{b,\,\text{frac},\,k} = \frac{c_{b,\,k}}{c_{b,\,\text{tot}}}$$

$$m_{b,\,\text{frac},\,k} = \frac{m_{b,\,k}}{m_{b,\,\text{tot}}}$$

$$s_{b,\,\text{frac},\,k} = \frac{s_{b,\,k}}{s_{b,\,\text{tot}}}$$

ODE Formulations for Surface Concentrations

The surface of a 1D geometry has a 0 dimension, hence no surface transport can be modeled and the governing equation is reduced to an ODE:

$$\frac{\partial c_{s,i}}{\partial t} = R_{s,i}$$

Surface Reaction Equations on Deforming Geometries

If a Surface Reaction interface is used in conjunction with a Deformed Geometry or a Moving Mesh (ale) interface, the boundary concentration can either be assumed to be transported with the deforming geometry (moving mesh), with no compensation for the stretching (the Compensate for boundary stretching check box is not selected), or the species can be assumed to "float" on the mesh (the Compensate for boundary stretching check box is selected, which is the default). In the latter case the following is assumed in regard to the coupling between the surface species and bulk species and the mesh movement:

- Expansion or contraction of the boundary dilutes or increases concentration of the species, respectively, so that the surface integral (in spatial coordinates) of the species is kept constant.
- Tangential mesh movement has no impact on the local concentration in spatial coordinates, that is, the tangential transport of surface and bulk species does not move with the mesh in the tangential direction.

In order to comply with the additional contributions to the mass balance, equations are added. First, the following terms are added to the right-hand side of Equation 3-106 and Equation 3-107, respectively.

$$-c_{s,i}\frac{\partial}{\partial t}\ln \partial A$$

$$-c_{b,k}\frac{\partial}{\partial t}\ln \partial A$$

where ∂A is the infinitesimal mesh area segment (area scale factor). The above terms account for the concentration change due to a fractional area change.

Second, the resulting unwanted tangential convection, imposed by the mesh movement, is compensated for by the adding following terms to the right-hand side of Equation 3-106 and Equation 3-107, respectively:

$$\nabla_t \cdot (c_{s,i}\mathbf{v}_{t,\text{mesh}})$$

$$\nabla_t \cdot (c_{b,k}\mathbf{v}_{t,\text{mesh}})$$

where $\mathbf{v}_{t,\text{mesh}}$ is the mesh velocity in the tangential direction.

This convectional term needs often to be stabilized using methods such as streamline diffusion or isotropic diffusion.

Reference for the Surface Reactions Interface

1. R.J. Kee, M.E. Coltrin, and P. Glarborg, *Chemically Reacting Flow*, chapter 11, John Wiley & Sons, 2003.

Theory for the Nernst–Planck Equations Interface

The Nernst–Planck Equations Interface theory is described in this section:

- Governing Equations for the Nernst–Planck Formulation
- Convective Term Formulation

Governing Equations for the Nernst–Planck Formulation

The following version of the Nernst–Planck equation treats transport by convection, diffusion, and migration of each dissolved species:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i \mathbf{u}) = -\nabla \cdot (-D_i \nabla c_i - u_{\mathrm{m},i} F c_i \nabla V) + R_i = -\nabla \cdot \mathbf{J}_i + R_i \qquad (3\text{-}108)$$

where $\mathbf{J}_i$ is the molar flux relative to the convective transport, and R_i (SI unit: mol/($\mathrm{m}^3 \cdot \mathrm{s}$)) is the reaction term. The velocity, $\mathbf{u}$, is equal to the velocity of the solvent. This implies that the solute's contribution to the solvent's velocity, through shear or any other forces, is negligible in comparison to the solvent's contribution to the solute. Equation 3-108 introduces one variable for the concentration of each of the dissolved species and the electric potential, V.

Apart from the transport equations, the physics interface assumes that the *electroneutrality condition* holds:

$$\sum z_i c_i = 0 \qquad (3\text{-}109)$$

that is that the net charge in every control volume is zero. This means that $Q - 1$, where Q is the number of species present, can be solved for using Equation 3-108. The remaining species concentration is computed from the electroneutrality condition. This means that boundary conditions for this species cannot be specified, although it takes part in the boundary condition descriptions for the current density. Often, the species chosen to be computed from electroneutrality is the oppositely charged ion, to the electroactive species, from a supporting electrolyte.

To compute the electric potential, taking the transport of every charged species into account, create the following linear combination of the n mass balance equations, where each mass balance equation is weighted with the factor Fz_i:

$$F\sum_{i=1}^{n} z_i \frac{\partial c_i}{\partial t} + \nabla \cdot \left(F\sum_{i=1}^{n} z_i \mathbf{N}_i \right) = F\sum_{i=1}^{n} z_i R_i \tag{3-110}$$

The first term in Equation 3-110 is zero, which can be shown by taking the time derivative of the electroneutrality condition. The expression under the divergence operator is the total current density vector, defined by:

$$\mathbf{i} = F\sum_{i=1}^{n} z_i(-D_i \nabla c_i - z_i u_{\mathrm{m},i} F c_i \nabla V) \tag{3-111}$$

Notice that no convective term is included in the expression for the current density, which is also a result of the electroneutrality condition.

It is now possible to rewrite Equation 3-110 as:

$$\nabla \cdot \mathbf{i} = F\sum_{i=1}^{n} z_i R_i \tag{3-112}$$

This equation states the conservation of electric charge and is the one solved for to compute the electric potential.

Equation 3-108, Equation 3-109, and Equation 3-112 are sufficient for describing the potential and concentration distribution in an electrochemical cell or in an electrolyte subjected to an electric field.

A useful observation from Equation 3-111 is that the ionic conductivity, defined in absence of concentration gradients, is implicitly given by:

$$\kappa = F^2 \sum_{i=1}^{n} z_i^2 c_i u_{\mathrm{m},i}$$

Furthermore, the potential gradient caused by the presence of a concentration gradient under situations with zero current becomes:

$$\nabla V = \frac{\sum_{i=1}^{n} (-D_i \nabla c_i)}{\sum_{i=1}^{n} z_i u_{\mathrm{m},i} F c_i}$$

In the field of electrochemistry, this is known as the junction potential.

Convective Term Formulation

When modeling mass transport in the Nernst–Planck Equations interface, two formulations are available for the convective term: a conservative and a nonconservative formulation. Equation 3-108 shows the conservative formulation.

In the nonconservative formulation the velocity is moved out of the divergence operator, which improves the stability of systems coupled to a momentum balance (fluid-flow equation). This is only applicable to systems that contain incompressible fluids. In these fluids, the following continuity equation is satisfied:

$$\nabla \cdot \mathbf{u} = 0 \tag{3-113}$$

and Equation 3-108 can be rewritten as:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i - z_i u_{\mathrm{m},i} F c_i \nabla V) + \mathbf{u} \cdot \nabla c_i = R_i \tag{3-114}$$

which can be called the nonconservative formulation and is the default formulation in the Nernst–Planck Equations interface.

Specify the equation formulation in the Advanced Settings section of the Nernst–Planck Equations interface.

Theory for the Reacting Laminar Flow Interface

The following sections describe theory applicable for the Reacting Flow interface:

- Pseudo Time Stepping for Mass Transport
- The Stefan Velocity
- The Chemical Reaction Rate

Pseudo Time Stepping for Mass Transport

In order to improve the solution robustness, pseudo time stepping can be used for the Transport of Concentrated Species interface when solving a stationary model. Using pseudo time stepping, a fictitious time derivative term:

$$\rho\frac{\omega_i - \text{nojac}(\omega_i)}{\tilde{\Delta t}}$$

is added to the left-hand side of the mass fraction equations. Here ρ is the fluid mixture density, ω_i is the mass fraction (dimensionless) of species i, and $\tilde{\Delta t}$ is the *pseudo time step*. Since ω_i–`nojac`(ω_i) is always zero, this term does not affect the final solution. It does, however, affect the discrete equation system and effectively transforms a nonlinear iteration into a time step of size $\tilde{\Delta t}$.

For a description of the pseudo time step term for the Navier-Stokes equations and the pseudo time step see Pseudo Time Stepping for Laminar Flow Models and Pseudo Time Stepping in the *COMSOL Multiphysics Reference Manual*.

The Stefan Velocity

Heterogeneous reactions on fluid-solid surfaces can affect the mass, momentum, and energy balances at the interface separating the fluid and the solid. On the reacting surface, the production or destruction rate, $r_{s,i}$ (SI unit: mol/(m^2·s)), of a fluid phase species is balanced by the total mass flux of the species. The mass balance for species i on a boundary representing a fluid-solid interface is given by:

$$\mathbf{n} \cdot (\mathbf{j}_i + \rho \omega_i \mathbf{u}) = r_{s,i} M_i \tag{3-115}$$

Here, $\mathbf{n}$ is the unit normal pointing out of the fluid domain, $\mathbf{u}$ is the mass averaged velocity of the fluid mixture (SI unit: m/s), $\mathbf{j}_i$ denotes the mass flux of species i relative to relative to the mixture (typically due to diffusion), and M_i is the species molar mass (SI unit: kg/mol). Summing the mass balances at the surface, over all species, results in an effective mixture velocity:

$$\mathbf{n} \cdot \rho \mathbf{u}_s = \sum_{i=1}^{N} r_{s,i} M_i \tag{3-116}$$

referred to as the Stefan velocity, here denoted $\mathbf{u}_s$. To reach Equation 3-116 the fact that the sum of all mass fractions is one, and that the sum of all relative diffusive fluxes is zero, was used.

Equation 3-116 implies that surface reactions result in a net flux between the surface and the domain. A net flux in turn corresponds to an effective convective velocity at the domain boundary; the Stefan velocity. It should be noted here that when solving for mass transport inside a fluid domain, an outer boundary of the domain corresponds to a position just outside of the actual physical wall (on the fluid side). The domain boundary does not coincide with the physical wall.

In most reacting flow models, the species mass fractions in the fluid domain are solved for without including the surface concentrations (mol per area) on exterior walls. One reason for this is that the surface reaction rates are often not known. In this case, surface reactions can be modeled either by applying a mass flux or prescribing the mass fraction, or a combination of both, on fluid boundaries adjacent to the reacting surface. The Stefan velocity on a fluid domain boundary is then defined as the net mass flux resulting from the boundary conditions applied:

$$\mathbf{n} \cdot \rho \mathbf{u}_s = \sum_{i=1}^{N} \mathbf{n} \cdot (\mathbf{j}_{0,i} + \rho \omega_{0,i} u) \tag{3-117}$$

Here, the first term contains contributions from boundary conditions prescribing the mass flux, while the second contains contributions from boundary conditions prescribing the mass fractions. Contributions to the Stefan velocity can be added by selecting **Account for Stefan velocity** in the Flux or Mass Fraction features in The Transport of Concentrated Species interface.

The resulting Stefan velocity based on mass transport boundary conditions is computed as:

$$\mathbf{n} \cdot \mathbf{u}_s = \frac{\sum_{i=1}^{N} \mathbf{n} \cdot \mathbf{j}_{0,i}}{\rho\left(1 - \sum_{i}^{N} \omega_{i,0}\right)} \tag{3-118}$$

Using a Reacting Flow interface, the Stefan velocity, defined in the manner of Equation 3-118, is automatically computed and applied on boundaries corresponding to walls in the coupled fluid flow interface. The Stefan velocity is prescribed in the wall normal direction on the wall selection.

The Chemical Reaction Rate

For laminar flow, or when the **Turbulent-reaction model** is set to **None** in a Reaction feature (in Transport of Concentrated Species), the default (Automatic) reaction rate used by the Reaction feature is based on the mass action law. Consider a general reaction belonging to a set of j reactions and involving i species:

$$\mathrm{aA} + \mathrm{bB} + \cdots \underset{k_j^r}{\overset{k_j^f}{\rightleftharpoons}} \mathrm{xX} + \mathrm{yY} + \cdots \tag{3-119}$$

For such a reaction set, the reaction rates r_j (SI unit: mol/(m^3·s)), can be described by the mass action law:

$$r_j = k_j^f \prod_{i \in \text{react}} c_i^{-\nu_{ij}} - k_j^r \prod_{i \in \text{prod}} c_i^{\nu_{ij}} \tag{3-120}$$

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 (SI unit: mol/m^3). The stoichiometric coefficients are denoted ν_{ij}, and are defined to be 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, the temperature dependence can be included by using the predefined Arrhenius expressions for the rate constants:

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

Here, A denotes the frequency factor, n the temperature exponent, E the activation energy (SI unit: 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 $(m^3/mol)^{\alpha-1}/s$, where α is the order of the reaction (with respect to the concentrations).

.

The Transport of Diluted Species Interface

The **Transport of Diluted Species (tds)** interface ( ), found under the **Chemical Species Transport** branch ( ), is used to calculate the concentration field of a dilute solute in a solvent. Transport and reactions of the species dissolved in a gas, liquid, or solid can be handled with this interface. The driving forces for transport can be diffusion by Fick's law, convection when coupled to a flow field, and migration, when coupled to an electric field.

The interface supports simulation of transport by convection and diffusion in 1D, 2D, and 3D as well as for axisymmetric components in 1D and 2D. The dependent variable is the molar concentration, c. Modeling multiple species transport is possible, whereby the physics interface solves for the molar concentration, c_i, of each species i.

SETTINGS

The **Label** is the default physics interface name.

The **Name** is used primarily as a scope prefix for variables defined by the physics interface. Refer to such physics interface variables in expressions using the pattern `<name>.<variable_name>`. In order to distinguish between variables belonging to different physics interfaces, the `name` string must be unique. Only letters, numbers, and underscores (_) are permitted in the **Name** field. The first character must be a letter.

The default **Name** (for the first physics interface in the model) is `tds`.

DOMAIN SELECTION

If any part of the model geometry should not partake in the mass transfer model, remove that part from the selection list.

TRANSPORT MECHANISMS

Mass transport due to diffusion is always included. Use the check boxes available under **Additional transport mechanisms** to control other transport mechanisms.

Note: Some of the additional transport mechanisms listed below are only available in certain products. For details see https://www.comsol.com/products/specifications/.

- By default, the **Convection** check box is selected. Clear the check box to disable convective transport.
- Select the **Migration in electric field** check box to activate transport of ionic species in an electric field. See further the theory section Adding Transport Through Migration.

Transport of ionic species in an electric field is available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

Mass Transport in Porous Media

The **Mass transport in porous media** check box activates functionality specific to species transport in porous media:

- Porous Medium
- Unsaturated Porous Medium
- Porous Electrode Coupling
- Reactive Pellet Bed
- Volatilization
- Species Source

Note: Mass transport in porous media is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

CONSISTENT STABILIZATION

To display this sections, click the **Show** button ( ) and select **Stabilization**.

- When the **Crosswind diffusion** check box is selected, a weak term that reduces spurious oscillations is added to the transport equation. The resulting equation system is always nonlinear. There are two options for the **Crosswind diffusion type**:
  - **Do Carmo and Galeão** — the default option. This type of crosswind diffusion reduces undershoots and overshoots to a minimum but can in rare cases give equation systems that are difficult to fully converge.
  - **Codina**. This option is less diffusive compared to the Do Carmo and Galeão option but can result in more undershoots and overshoots. It is also less effective for anisotropic meshes. The Codina option activates a text field for the **Lower gradient limit** g_{lim}. It defaults to `0.1[mol/m^3)/tds.helem`, where `tds.helem` is the local element size.
- For both consistent stabilization methods, select an **Equation residual**. **Approximate residual** is the default and means that derivatives of the diffusion tensor components are neglected. This setting is usually accurate enough and is computationally faster. If required, select **Full residual** instead.

INCONSISTENT STABILIZATION

To display this section, click the **Show** button ( ) and select **Stabilization**. By default, the **Isotropic diffusion** check box is not selected, because this type of stabilization adds artificial diffusion and affects the accuracy of the original problem. However, this option can be used to get a good initial guess for under resolved problems.

ADVANCED SETTINGS

To display this section, click the **Show** button ( ) and select **Advanced Physics Options**. Normally these settings do not need to be changed. Select a **Convective term** — **Nonconservative form** (the default) or **Conservative form**. The conservative formulation should be used for compressible flow. See Convective Term Formulation for more information.

DISCRETIZATION

To display all settings available in this section, click the **Show** button ( ) and select **Advanced Physics Options**.

The **Compute boundary fluxes** check box is activated by default so that COMSOL Multiphysics computes predefined accurate boundary flux variables. When this option

is checked, the solver computes variables storing accurate boundary fluxes from each boundary into the adjacent domain.

If the check box is cleared, the COMSOL Multiphysics software instead computes the flux variables from the dependent variables using extrapolation, which is less accurate in postprocessing results but does not create extra dependent variables on the boundaries for the fluxes.

The flux variables affected in the interface are:

- `ndflux_c` (where `c` is the dependent variable for the concentration). This is the normal diffusive flux and corresponds to the boundary flux when diffusion is the only contribution to the flux term.
- `ntflux_c` (where `c` is the dependent variable for the concentration). This is the normal total flux and corresponds to the boundary flux plus additional transport terms, for example, the convective flux when you use the nonconservative form.

Also the **Apply smoothing to boundary fluxes** check box is available if the previous check box is checked. The smoothing can provide a more well-behaved flux value close to singularities.

For details about the boundary fluxes settings, see Computing Accurate Fluxes in the *COMSOL Multiphysics Reference Manual*.

The **Value type when using splitting of complex variables** setting should in most pure mass transfer problems be set to **Real**, which is the default. It makes sure that the dependent variable does not get affected by small imaginary contributions, which can occur, for example, when combining a Time Dependent or Stationary study with a frequency-domain study. For more information, see Splitting Complex-Valued Variables in the *COMSOL Multiphysics Reference Manual*.

DEPENDENT VARIABLES

The dependent variable name is the **Concentration** c by default. The names must be unique with respect to all other dependent variables in the component.

Add or remove species variables in the model and also change the names of the dependent variables that represent the species concentrations.

Enter the **Number of species**. Use the **Add concentration** (+) and **Remove concentration** ( ) buttons as needed.

FURTHER READING

- Theory for the Transport of Diluted Species Interface
- Numerical Stabilization in the *COMSOL Multiphysics Reference Manual*.
- In the *COMSOL Multiphysics Reference Manual*, see Table 2-4 for links to common sections and Table 2-5 for common feature nodes. You can also search for information: press F1 to open the **Help** window or Ctrl+F1 to open the **Documentation** window.

- *Effective Diffusivity in Porous Materials*: Application Library path **COMSOL_Multiphysics/Diffusion/effective_diffusivity**
- *Micromixer*: Application Library path **COMSOL_Multiphysics/Fluid_Dynamics/micromixer**

The Transport of Diluted Species in Porous Media Interface

This interface ( ), found under the **Chemical Species Transport** branch ( ), is used to calculate the species concentration and transport in free and porous media. The interface is the same as the *Transport of Diluted Species* interface but it uses other defaults: The Mass Transport in Porous Media property is selected, and a Porous Medium node is added by default. The interface includes reaction rate expressions and solute sources for modeling of species transport and reaction in porous media.

This interface is dedicated to modeling transport in porous media, including immobile and mobile phases, where the chemical species may be subjected to diffusion, convection, migration, dispersion, adsorption, and volatilization in porous media. It supports cases where either the solid phase substrate is exclusively immobile, or when a gas-filling medium is also assumed to be immobile.

It applies to one or more diluted species or solutes that move primarily within a fluid that fills (saturated) or partially fills (unsaturated) the voids in a solid porous medium. The pore space not filled with fluid contains an immobile gas phase. Models including a combination of porous media types can be studied.

The main feature nodes are the **Porous Medium** and **Unsaturated Porous Medium** nodes, which add the equations for the species concentrations and provide an interface for defining the properties of the porous media, as well as additional properties governing

adsorption, volatilization, dispersion and diffusion, migration, and the velocity field to model convection.

The physics interface can be used for stationary and time-dependent analysis.

When this physics interface is added, these default nodes are also added to the **Model Builder** — **Porous Medium**, **No Flux** (the default boundary condition), and **Initial Values**. Then, from the **Physics** toolbar, add other nodes that implement, for example, boundary conditions, reaction rate expressions, and species sources. You can also right-click **Transport of Diluted Species in Porous Media** to select physics features from the context menu.

SETTINGS

The rest of the settings are the same as The Transport of Diluted Species Interface.

FURTHER READING

- Mass Balance Equation for Transport of Diluted Species in Porous Media
- Domain, Boundary, and Pair Nodes for the Transport of Diluted Species Interface

- *Variably Saturated Flow and Transport — Sorbing Solute*: Application Library path **Subsurface_Flow_Module/Solute_Transport/sorbing_solute**

  Web link: https://www.comsol.com/model/variably-saturated-flow-and-transport-sorbing-solute-490

Domain, Boundary, and Pair Nodes for the Transport of Diluted Species Interface

The Transport of Diluted Species Interface has the following domain, boundary, and pair nodes, listed in alphabetical order, available from the **Physics** ribbon toolbar

(Windows users), **Physics** context menu (Mac or Linux users), or by right-clicking to access the context menu (all users).

To add a node, go to the **Physics** toolbar, no matter what operating system you are using. Subnodes are available by clicking the parent node and selecting it from the **Attributes** menu.

- Adsorption
- Concentration
- Dispersion
- Electrode Surface Coupling
- Equilibrium Reaction
- Fast Irreversible Surface Reaction
- Fluid
- Flux
- Flux Discontinuity
- Fracture
- Gas
- Inflow
- Initial Values
- Line Mass Source
- Liquid
- Mass-Based Concentrations
- No Flux
- Open Boundary
- Outflow
- Partition Condition
- Periodic Condition
- Point Mass Source
- Porous Matrix
- Porous Medium
- Porous Media Diffusion
- Porous Electrode Coupling
- Reaction Coefficients
- Reactions
- Reactions (Reactive Pellet Bed)
- Reactive Pellet Bed
- Species Source
- Surface Reactions
- Surface Equilibrium Reaction
- Symmetry
- Thin Diffusion Barrier
- Thin Impermeable Barrier
- Transport Properties
- Turbulent Mixing
- Unsaturated Porous Medium
- Volatilization

Some features require certain add-on modules. For details see https://www.comsol.com/products/specifications/

For axisymmetric components, COMSOL Multiphysics takes the axial symmetry boundaries (at $r = 0$) into account and automatically adds an **Axial Symmetry** node that is valid on boundaries representing the symmetry axis.

In the *COMSOL Multiphysics Reference Manual*, see Table 2-4 for links to common sections and Table 2-5 for common feature nodes. You can also search for information: press F1 to open the **Help** window or Ctrl+F1 to open the **Documentation** window.

Transport Properties

The settings in this node are dependent on the check boxes selected under Transport Mechanisms on the Settings window for the Transport of Diluted Species interface. It includes only the sections required by the activated transport mechanisms. It has all the equations defining transport of diluted species as well as inputs for the material properties.

When the **Convection** check box is selected, the Turbulent Mixing subnode is available from the context menu as well as from the **Physics** toolbar, **Attributes** menu.

MODEL INPUTS

The temperature model input is always available. Select the source of the **Temperature**. For **User defined**, enter a value or expression for the temperature in the input field. This input option is always available.

You can also select the temperature solved for by a Heat Transfer interface added to the model component. These physics interfaces are available for selection in the **Temperature** list.

CONVECTION

If transport by convection is active, the velocity field of the solvent needs to be specified. Select the source of the **Velocity field**. For **User defined**, enter values or expressions for the velocity components in the input fields. This input option is always available.

You can also select the velocity field solved for by a Fluid Flow interface added to the model component. These physics interfaces are available for selection in the **Velocity field** list.

DIFFUSION

Use this section to specify diffusion coefficients describing the diffusion of each species in the solvent fluid.

Use the **Source** list to select to pick up diffusion coefficients defined in a material or a Chemistry interface.

Select **Material**, and a **Fluid material** to use a diffusion coefficient in a material available in the model. User-defined property groups including a diffusion coefficient output property are available for selection in the **Fluid diffusion coefficient** list.

Select **Chemistry** to use a diffusion coefficient from a Chemistry interface added to model component. Diffusion coefficients are automatically defined when **Calculate transport properties** is selected on the interface level of a Chemistry interface. All defined diffusion coefficients are available for selection in the **Fluid diffusion coefficient** list.

For **User defined**, enter a value or expression for the **Fluid diffusion coefficient** D_c of each species in the corresponding input field. This can be a scalar value for isotropic diffusion or a tensor describing anisotropic diffusion. Select the appropriate tensor type — **Isotropic**, **Diagonal**, **Symmetric**, or **Full** that describes the diffusion transport, and then enter the values in the corresponding element (one value for each species).

Note that multiple species, as well as Migration in Electric fields (described below) is only available for certain COMSOL Multiphysics add-on products. See details: https://www.comsol.com/products/specifications/.

MIGRATION IN ELECTRIC FIELD

This section is available when the **Migration in electric field** check box is selected. From the **Electric potential** list, select the source of the electric field.

- Enter a value or expression for the **Electric potential** V, which is **User defined**; this input option is always available.
- Select the electric potential solved by an AC/DC-based interface that has also been added to the model.
- Select the electric potential defined or solved by Electrochemistry interface that has been added to the component.

By default the **Mobility** is set to be calculated based on the species diffusivity and the temperature using the **Nernst-Einstein relation**. For **User defined**, and under **Mobility**, select the appropriate scalar or tensor type — **Isotropic**, **Diagonal**, **Symmetric**, or **Full** — and type in the value of expression of the mobility $u_{m,c}$.

Enter the **Charge number** z_c (dimensionless, but requires a plus or minus sign) for each species.

The temperature (if you are using mobilities based on the Nernst-Einstein relation) is taken from **Model Inputs** section.

Note that the migration in electric fields feature is only available in some COMSOL products. See details: https://www.comsol.com/products/specifications/.

EXAMPLE MODELS

- *Separation Through Dialysis*: Application Library path **Chemical_Reaction_Engineering_Module/Mixing_and_Separation/dialysis**

  Web link: https://www.comsol.com/model/separation-through-dialysis-258

- *Transport in an Electrokinetic Valve*: Application Library path **Microfluidics_Module/Fluid_Flow/electrokinetic_valve**

  Web link: https://www.comsol.com/model/electrokinetic-valve-603

Turbulent Mixing

Use this node to account for the turbulent mixing of the chemical species caused by the eddy diffusivity. This node should typically be used when the specified velocity field corresponds to a RANS solution.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

The subnode can added from the context menu (right-click the Transport Properties parent node), as well as from the **Physics** toolbar, **Attributes** menu, provided that **Convection** is selected as a transport mechanism.

TURBULENT MIXING PARAMETERS

Some physics interfaces provide the turbulent kinematic viscosity, and these appear as options in the **Turbulent kinematic viscosity** ν_T list. The list always contains the **User defined** option where any value or expression can be entered.

The default **Turbulent Schmidt number** Sc_T is 0.71 (dimensionless).

FURTHER READING

See the section About Turbulent Mixing in the *CFD Module User's Guide* (this link is available online or if you have the CFD Module documentation installed).

Initial Values

The **Initial Values** node specifies the initial values for the concentration of each species. These serve as an initial guess for a stationary solver or as initial conditions for a transient simulation.

DOMAIN SELECTION

If there are several types of domains with different initial values defined, it might be necessary to remove some domains from the selection. These are then defined in an additional **Initial Values** node.

INITIAL VALUES

Enter a value or expression for the initial value of the **Concentration** or concentrations, c_i. This also serves as a starting guess for stationary problems.

Mass-Based Concentrations

Use the **Mass-Based Concentrations** node to add postprocessing variables for mass-based concentrations (SI unit: kg/m^3) and mass fractions (dimensionless) for all species.

MIXTURE PROPERTIES

The default **Solvent density** $\rho_{solvent}$ is taken **From material**. For **User defined,** enter a value or expression manually. Define the **Molar mass** of each species, which is needed to calculate the mass-based concentration.

Reactions

Use the **Reactions** node to account for the consumption or production of species through chemical reactions. Define the rate expressions as required.

DOMAIN SELECTION

From the **Selection** list, choose the domains on which to define rate expression or expressions that govern the source term in the transport equations.

Several reaction nodes can be used to account for different reactions in different parts for the modeling geometry.

REACTION RATES

Add a rate expression R (SI unit: mol/(m^3·s)) for species i. Enter a value or expression in the field. Note that if you have the *Chemistry* interface available, provided with the *Chemical Reaction Engineering Module*, the reaction rate expressions can be automatically generated and picked up using the drop-down menu. For an example, see the application *Fine Chemical Production in a Plate Reactor* as linked below.

REACTING VOLUME

This section is only available when the Mass Transport in Porous Media property is available and selected. See https://www.comsol.com/products/specifications/ for more details on availability.

When specifying reaction rates for a species in porous media, the specified reaction rate may have the basis of the total volume, the pore volume, or the volume of a particular phase.

- For **Total volume**, the reaction expressions in mol/(m^3·s) are specified per unit volume of the model domain (multiplied by unity).
- For **Pore volume**, the reaction expressions in mol/(m^3·s) are specified per unit volume of total pore space. The reaction expressions will be multiplied by the domain porosity, ε_p. (ε_p equals unity for nonporous domains.)
- For **Liquid phase**, the reaction expressions in mol/(m^3·s) are specified per unit volume of liquid in the pore space. The expressions will be multiplied by the liquid volume fraction θ. (θ equals ε_p for Saturated Porous Media domains).
- For **Gas phase**, the expressions are multiplied by the gas volume fraction $\alpha_v = \varepsilon_p - \theta$. α_v equals 0 for Saturated Porous Media domains.

FURTHER READING

See the theory chapter on chemical species transport, starting with the section *Mass Balance Equation*.

- *Fine Chemical Production in a Plate Reactor*: Application Library path **Chemical_Reaction_Engineering_Module/ Reactors_with_Mass_and_Heat_Transfer/plate_reactor**

  Web link: https://www.comsol.com/model/fine-chemical-production-in-a-plate-reactor-8589

No Flux

This node is the default boundary condition on exterior boundaries. It should be used on boundaries across which there is no mass flux, typically solid walls where no surface reactions occur. The condition applied for each species corresponds to

$$-\mathbf{n} \cdot (-D\nabla c) = 0$$

where $\mathbf{n}$ denotes the outward pointing normal of the boundary. When the mass transport includes migration of ionic species, the no flux condition is:

$$-\mathbf{n} \cdot (-D\nabla c - zu_{\mathrm{m}}Fc\nabla\phi) = 0$$

CONVECTION

By default, the feature prescribes a vanishing flux due to diffusion and migration in an electric field. This is the appropriate no flux condition when the relative convective velocity at the boundary is zero. When the fluid velocity at the boundary is not equal to that of the boundary, it is often convenient to prescribe the total flux including the convection. To do this select **Include** in the **Convection** section.

When including the convection, the no flux condition prescribed is

$$-\mathbf{n} \cdot (-D\nabla c + \mathbf{u}c) = 0$$

or

$$-\mathbf{n} \cdot (-D\nabla c - zu_{\mathrm{m}}Fc\nabla\phi + \mathbf{u}c) = 0$$

when migration of ionic species is included.

Inflow

Use this node to specify all species concentrations at an inlet boundary.

If you want to specify the concentration of a subset of the partaking species, this can be done by using the Concentration node instead.

For the **Electroanalysis** interface, this node is available when you select the **Convection** check box on the physics interface **Settings** window.

CONCENTRATION

For the concentration of each species $c_{0,c}$ (SI unit: $\mathrm{mol/m^3}$), enter a value or expression.

BOUNDARY CONDITION TYPE

The option **Concentration constraint** constrains the concentration values on the boundary by the use of pointwise constraints.

The other option, **Flux (Danckwerts)** can be used when the concentration at the boundary is not known, or when it varies in a non-trivial manner. This may, for example, be useful when reactions with high reaction rates occur in the vicinity of the inlet. In this case the concentration far upstream of the boundary is instead prescribed. The **Flux (Danckwerts)** condition prescribes the total flux defined by the upstream concentration and the fluid velocity at the boundary.

CONSTRAINT SETTINGS

To display this section, click the **Show** button ( ) and select **Advanced Physics Options**. You can find details about the different constraint settings in the section Constraint Reaction Terms in the *COMSOL Multiphysics Reference Manual*.

FURTHER READING

See the theory chapter in the section Danckwerts Inflow Boundary Condition.

Outflow

Apply this condition at outlets boundaries where species should be transported out of the model domain by fluid motion or by an electric field (in the case of ions). It is assumed that convection and migration (in an electric field) are the dominating transport mechanisms across the boundary, and therefore that the diffusive transport can be ignored, that is:

$$\mathbf{n} \cdot (-D\nabla c) = 0$$

Note that the **Convection** or the **Migration in electric field** transport mechanisms needs to be included for this node to be available.

Concentration

This condition node adds a boundary condition for the species concentration. For example, a $c = c_0$ condition specifies the concentration of species c.

CONCENTRATION

Individually specify the concentration for each species. Select the check box for the **Species** to specify the concentration, and then enter a value or expression in the corresponding field. To use another boundary condition for a specific species, click to clear the check box for the concentration of that species.

CONSTRAINT SETTINGS

To display this section, click the **Show** button ( ) and select **Advanced Physics Options**. You can find details about the different constraint settings in the section Constraint Reaction Terms in the *COMSOL Multiphysics Reference Manual*.

Flux

This node can be used to specify the species molar flux across a boundary. The flux can for example occur due to chemical reactions or a phase change at the boundary. The flux can also represent the transport to or from a surrounding environment currently not included model.

The prescribed flux of a species c is by default defined as

$$-\mathbf{n} \cdot (-D\nabla c) = J_0$$

where $\mathbf{n}$ denotes the outward pointing normal of the boundary. When the mass transport includes migration of ionic species, the flux is defined as:

$$-\mathbf{n} \cdot (-D\nabla c - zu_m Fc\nabla\phi) = J_0$$

The flux prescribed, J_0, can include any arbitrary user-specified expression. It can be constant or a function of a dependent variable or independent variable. Common examples are a flux dependent of the concentration, temperature, pressure or the electric potential ϕ.

CONVECTION

By default, the flux due to diffusion and migration in an electric field is prescribed. This is the appropriate flux condition when the relative velocity at the boundary is zero. When the fluid velocity is not equal to that of the boundary, it is often convenient to prescribe the total flux, including the convection. To do this select **Include** in the **Convection** section.

When including the convection, the prescribed flux is defined as:

$$-\mathbf{n} \cdot (-D\nabla c + \mathbf{u}c) = J_0$$

or

$$-\mathbf{n} \cdot (-D\nabla c - zu_{\mathrm{m}}Fc\nabla\phi + \mathbf{u}c) = J_0$$

when migration of ionic species is included.

INWARD FLUX

Select the Species check box for the species for which to specify the flux, and enter a value or expression for the inward flux in the corresponding field. Use a minus sign when specifying a flux directed out of the system. To use another boundary condition for a specific species, click to clear the check box for that species.

External convection

Set **Flux type** to **External convection** to prescribe a flux to or from an exterior domain (not modeled) assumed to include convection. The exterior can for example include a forced convection to control the temperature or to increase the mass transport. In this case the prescribed mass flux corresponds to

$$J_0 = k_{\mathrm{c}}(c_{\mathrm{b}} - c)$$

where k_{c} is a mass transfer coefficient and c_{b} is the bulk concentration, the typical concentration far into the surrounding exterior domain.

Symmetry

The **Symmetry** node can be used to represent boundaries where the species concentration is symmetric, that is, where there is no mass flux across the boundary.

This boundary condition is identical to that of the No Flux node.

Flux Discontinuity

This node represents a discontinuity in the mass flux across an interior boundary:

$$-\mathbf{n}\cdot[(\mathbf{J}+\mathbf{u}c)_{\mathrm{u}}-(\mathbf{J}+\mathbf{u}c)_{\mathrm{d}}] = N_0 \qquad \mathbf{J} = -D\nabla c - zu_{\mathrm{m}}Fc\nabla\phi$$

where the value N_0 (SI unit: mol/(m^2·s)) specifies the jump in total flux at the boundary. This can be used to model a boundary source, for example a surface reaction, adsorption or desorption.

FLUX DISCONTINUITY

In this section the jump in species flux (or surface source) is specified.

Select the Species check box for the species to specify and enter a value or expression for the material flux jump in the corresponding field. To use a different boundary condition for a specific species, click to clear the check box for the flux discontinuity of that species.

Partition Condition

The **Partition Condition** node can be used to prescribe the ratio between the concentration of a solute species in two different immiscible phases. It can for example be used on interior boundaries separating two liquid phases, a gas-liquid interface, or on a boundary separating a liquid phase and a solid or porous media. For a species concentration c_i, the ratio between the concentration on the up side and on the down side of the boundary ($c_{i,\mathrm{u}}$ and $c_{i,\mathrm{d}}$ respectively) is defined as

$$K_i = \frac{c_{i,\mathrm{u}}}{c_{i,\mathrm{d}}}$$

in terms of a partition coefficient K_i. The up and down side of the selected boundary is indicated in the Graphics window. The arrows point from the down side into the up side.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

PARTITION COEFFICIENT

Select the **Reverse direction** check box to reverse the direction of the arrows on the selected boundaries, and the corresponding definition of the up and down side concentration.

Use the associated input fields to prescribe the partition coefficient K_i.

FURTHER READING

For an example of using a partition condition, see this application example:

Separation Through Dialysis: Application Library path **Chemical_Reaction_Engineering_Module/Mixing_and_Separation/dialysis**

Periodic Condition

The **Periodic Condition** node can be used to define periodicity for the mass transport between two sets of boundaries. The node prescribes continuity in the concentration and the mass flux between the "source" and the "destination" side respectively. Note that these names are arbitrary and does not influence the direction in which mass is transported. It is dictated by mass transfer equations in the adjacent domains.

The node can be activated on more than two boundaries, in which case the feature tries to identify two separate surfaces that each consist of one or several connected boundaries.

For more complex geometries, it might be necessary to add the **Destination Selection** subnode, which is available from the context menu (right-click the parent node) as well as from the **Physics** toolbar, **Attributes** menu. With this subnode, the boundaries that constitute the source and destination surfaces can be manually specified.

FURTHER READING

For an example of using a periodic condition, see this application example:

The KdV Equation and Solitons: Application Library path **COMSOL_Multiphysics/Equation_Based/kdv_equation**

Line Mass Source

The **Line Mass Source** feature models mass flow originating from a tube or line region with an infinitely small radius.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

SELECTION

The **Line Mass Source** feature is available for all dimensions, but the applicable selection differs between the dimensions.

MODEL DIMENSION	APPLICABLE GEOMETRICAL ENTITY
2D	Points
2D Axisymmetry	Points not on the symmetry axis and the symmetry axis
3D	Edges

SPECIES SOURCE

Enter the source strength, $\dot{q}_{l,c}$, for each species (SI unit: mol/(m·s)). A positive value results in species injection from the line into the computational domain, and a negative value means that the species is removed from the computational domain.

Line sources located on a boundary affect the adjacent computational domains. This effect makes the physical strength of a line source located in a symmetry plane twice the given strength.

FURTHER READING

See the section Mass Sources for Species Transport.

Point Mass Source

The **Point Mass Source** feature models mass flow originating from an infinitely small domain around a point.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

SPECIES SOURCE

Enter the source strength, $\dot{q}_{p,c}$, for each species (SI unit: mol/s). A positive value results in species injection from the point into the computational domain, and a negative value means that the species is removed from the computational domain.

Point sources located on a boundary or on an edge affect the adjacent computational domains. This has the effect, for example, that the physical strength of a point source located in a symmetry plane is twice the given strength.

FURTHER READING

See the section Mass Sources for Species Transport.

Open Boundary

Use this node to set up mass transport across boundaries where both convective inflow and outflow can occur. On the parts of the boundary where fluid flows into the domain, an exterior species concentration is prescribed. On the remaining parts, where fluid flows out of the domain, a condition equivalent to the **Outflow** node is instead prescribed.

The direction of the flow across the boundary is typically calculated by a fluid flow interface and is provided as a model input to the Transport of Diluted Species interface.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

EXTERIOR CONCENTRATION

Enter a value or expression for the **Exterior concentration**.

Thin Diffusion Barrier

Use this boundary condition to model a thin layer through which mass is transported by diffusion only. The node is applicable on interior boundaries and can be used to avoid meshing thin structures.

THIN DIFFUSION BARRIER

Specify the **Layer thickness**, d_s, and input a **Diffusion coefficient**, $D_{s,c}$, for each of the species included.

Thin Impermeable Barrier

This feature models a thin mass transfer barrier. It is available on interior boundaries and introduces a discontinuity in the concentration across the boundary. On each side, a no-flux condition is prescribed for the mass transport implying that it acts as a barrier. The feature can be used to avoid meshing thin structures.

Solving a model involving coupled fluid flow and mass transfer, the Thin Impermeable Barrier feature can be combined with an Interior Wall feature in order to model a thin solid wall.

Equilibrium Reaction

Use this node to model a reaction where the kinetics is assumed so fast that the equilibrium condition is fulfilled at all times. The node solves for an additional degree of freedom (the reaction rate R_{eq}) to fulfill the equilibrium condition at all times in all space coordinates.

If the **Apply equilibrium condition on inflow boundaries** check box is selected, the specified inflow concentration values in all active **Inflow** boundary nodes for the physics interface are modified to comply with the equilibrium condition.

- A necessary requirement for this is feature to be available is that two or more species are solved for by the interface.
- This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

EQUILIBRIUM CONDITION

The list defaults to **Equilibrium constant** or select **User defined**. For either option, the **Apply equilibrium condition on inflow boundaries** check box is selected by default.

For **Equilibrium constant**, enter an **Equilibrium constant** K_{eq} (dimensionless). Also enter a value or expression for the **Unit activity concentration** C_{a0} (SI unit: $\mathrm{mol/m^3}$).

Selecting **Equilibrium constant** defines an equilibrium condition based on the stoichiometric coefficients, the species activities, and the law of mass action.

For **User defined**, enter an **Equilibrium expression** E_{eq} (dimensionless).

STOICHIOMETRIC COEFFICIENTS

Enter a value for the stoichiometric coefficient ν_c (dimensionless). The default is 0. Use negative values for reactants and positive values for products in the modeled reaction.

Species with a stoichiometric coefficient value of 0 are not affected by the **Equilibrium Reaction** node.

FURTHER READING

See

- Equilibrium Reaction Theory

Surface Reactions

The **Surface Reactions** node can be used to account for the species boundary flux due to chemical reactions occurring on a surface (heterogeneous reactions). For a domain species participating in a surface reaction, the boundary flux corresponds to the reaction rate at the surface.

SURFACE REACTION RATE

Specify the surface reaction rate J_0 of each species resulting from the reactions. Note that if you have the Chemistry interface available, provided with the Chemical Reaction Engineering Module, the reaction rate expressions can be automatically generated and picked up using the drop-down menu.

FURTHER READING

For an example of using the Surface Reactions node, see this application example:

	Chemical Vapor Deposition of GaAs: Application Library path **Chemical_Reaction_Engineering_Module/ Reactors_with_Mass_and_Heat_Transfer/gaas_cvd**

Surface Equilibrium Reaction

Use this node to model an equilibrium reaction on a boundary (surface). The settings for this node are similar to Equilibrium Reaction. Note that a necessary requirement for this is feature to be available is that two or more species are solved for by the interface.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

Fast Irreversible Surface Reaction

This boundary node defines an irreversible reaction where the kinetics is so fast that the only factor limiting the reaction rate is the transport of a species to the reacting surface.

The node will set the **Rate limiting species concentration to zero** at the boundary, and balance the fluxes of the species participating in the reaction and the current densities according to the Stoichiometric Coefficients settings.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

Porous Electrode Coupling

Use this node to add a molar source in a domain that is coupled to one or multiple Porous Electrode Reaction nodes of an Electrochemistry Interface.

The molar source is calculated from the number of electrons, stoichiometric coefficients, and volumetric current densities of the coupled porous electrode reactions specified in the **Reaction Coefficients** subnodes.

In the Transport of Concentrated Species interface, the molar sources (or sinks) are multiplied by the species molar masses to obtain the corresponding mass sources.

Additional Reaction Coefficients subnodes are available from the context menu (right-click the parent node) as well as from the **Physics** toolbar, **Attributes** menu.

Note that if you are also modeling the momentum transport and expect a nonnegligible total mass source or sink, which is often the case in gas diffusion electrodes, you need to also add a corresponding Porous Electrode Coupling node in the Fluid Flow interface.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

Reaction Coefficients

Add this node to the Electrode Surface Coupling and Porous Electrode Coupling features to define molar fluxes and sources based on electrode current densities in an **Electrochemistry** interface.

The molar flux or source is proportional to the stoichiometric coefficients and the current density according to Faraday's law.

Current densities from **Electrode Reaction** (i_{loc}, SI unit: A/m^2) or **Porous Electrode Reaction** nodes (i_{v}, SI unit: A/m^3) of any **Electrochemistry** interface in the model are available for selection as the **Coupled reaction**, and user-defined expressions are also supported.

Enter the **Number of participating electrons** n_m (dimensionless) and the **Stoichiometric coefficient** v_c (dimensionless) as explained in the theory section linked below.

Use multiple subnodes to couple to multiple reactions.

Electrode Surface Coupling

Use this node to define a flux boundary condition based on current densities of one or multiple Electrode Reaction nodes in an Electrochemistry interface.

The flux is proportional to the current densities and the stoichiometric coefficients according to Faraday's law as defined by summation over the Reaction Coefficients subnodes.

Note that if you are also modeling the momentum transport and expect a nonnegligible total mass flux over the boundary, which is often the case for gas

diffusion electrodes, you need to also add a corresponding Electrode Surface Coupling node in the Fluid Flow interface.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

Porous Medium

Use this node to model the concentration of diluted species transported by a solvent (mobile fluid phase) through interstices in a solid porous medium. In addition to transport due to convection and diffusion, the node contains functionality to include species evolution through adsorption and dispersion.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

Species transport through a porous medium is affected both by properties of fluid phase, and as well as properties of the solid matrix. These properties are defined in the Fluid and Porous Matrix subnodes respectively. The Porous Medium node supports material properties using a Porous Material node (described in the *COMSOL Multiphysics Reference Manual)*, where properties are defined per phase in a similar manner.

Add an Adsorption or a Dispersion subfeature to the **Porous Medium** to account for the corresponding transport mechanism.

Fluid

Use this node to specify the mass transfer in the mobile fluid solvent filling the pores of the Porous Medium.

MODEL INPUTS

The temperature model input is always available. By default, the **Temperature** model input is set to **Common model input**, and the temperature is controlled from Default Model Inputs under **Global Definitions** or by a locally defined Model Input. If a Heat Transfer interface is included in the component, it controls the temperature **Common**

model input. Alternatively, the temperature field can be selected from another physics interface. All physics interfaces have their own tags (**Name**). For example, if a Heat Transfer in Fluids interface is included in the component, the **Temperature (ht)** option is available for T.

You can also select **User defined** from the **Temperature** model input in order to manually prescribe T.

CONVECTION

If transport by convection is active, the velocity field of the solvent needs to be specified. For **User defined**, enter values or expressions for the velocity components in the input fields. This input option is always available. You can also select the velocity field solved for by a Fluid Flow interface added to the model component. These physics interfaces are available for selection in the **Velocity field** list.

DIFFUSION

Use this section to specify diffusion coefficients describing the diffusion of each species in the solvent fluid.

Use the **Source** list to select to pick up diffusion coefficients defined in a material or a Chemistry interface.

Select **Material**, and a **Fluid material** to use a diffusion coefficient in a material available in the model. User-defined property groups including a diffusion coefficient output property are available for selection in the **Fluid diffusion coefficient** list.

Select **Chemistry** to use a diffusion coefficient from a Chemistry interface added to model component. Diffusion coefficients are automatically defined when **Calculate transport properties** is selected on the interface level of a Chemistry interface. All defined diffusion coefficients are available for selection in the **Fluid diffusion coefficient** list.

For **User defined**, enter a value or expression for the **Fluid diffusion coefficient** $D_{\mathrm{F,i}}$ of each species in the corresponding input field.

In a porous medium the diffusivity is reduced due to the fact that the solid grains impede Brownian motion. Select an **Effective diffusivity model** to account for the reduced diffusivity. The available models are **Millington and Quirk model** (the default), **Bruggeman model**, **Tortuosity model**, or **No correction**. For **Tortuosity model**, enter a value for the tortuosity $\tau_{\mathrm{F,i}}$ (dimensionless).

Note that multiple species, as well as Migration in Electric fields (described below) is only available for certain COMSOL Multiphysics add-on products. See details: https://www.comsol.com/products/specifications/.

MIGRATION IN ELECTRIC FIELD

This section is available when the **Migration in electric field** check box is selected. From the **Electric potential** list, select the source of the electric field.

- For **User defined,** enter a value or expression for the **Electric potential** V. This input option is always available.
- Select the electric potential solved by an AC/DC-based interface that has added to the component.
- Select the electric potential defined or solved for by an Electrochemistry interface added to the component.

By default the **Mobility** is set to be calculated based on the species effective diffusivity and the temperature using the **Nernst-Einstein relation**. For **User defined**, select the appropriate scalar or tensor type — **Isotropic**, **Diagonal**, **Symmetric**, or **Full** — and type in the value or expression of the effective mobility $u_{\mathrm{me,i}}$.

Enter the **Charge number** z_{c} for each species.

Porous Matrix

This node sets the porosity when modeling transport of diluted species in a Porous Medium or a Unsaturated Porous Medium.

The default **Porosity** ε_{p} of the solid matrix is taken **From material**. The Porous Matrix node supports the use of a **Porous Material** node, where the porosity is defined in the manner of

$$\varepsilon_{\mathrm{p}} = 1 - \sum_{i} \theta_{\mathrm{s},i} - \sum_{i} \theta_{\mathrm{imf},i}$$

where $\theta_{\mathrm{s},i}$ and $\theta_{\mathrm{imf},i}$ are the porosities of the **Solid** and **Immobile Fluids** subnodes under the **Porous Material** node.

Select **From pellet bed densities** to compute the porosity using the (dry bulk) **Bed density** ρ_{b} and the (single phase) **Pellet density** ρ_{pe}. The porosity is then defined from

$$\varepsilon_p = 1 - \frac{\rho_b}{\rho_{pe}}$$

For **User defined**, enter a value or expression for the porosity.

Dispersion

Local variations in the velocity as the fluid flows around solid particles lead to mechanical mixing, referred to as dispersion. Use this feature to account for dispersion in a Porous Medium or a Unsaturated Porous Medium

This subfeature is available when both the **Mass transfer in porous media mass transfer** check box and the **Convection** check box are selected on the **Settings** window for the physics interface.

Select the **Specify dispersion for each species individually** check box to specify the dispersion tensor D_D (SI unit: m^2/s) for each species separately. When not selected the same dispersion tensor D_D is used for all species.

Select an option from the **Dispersion tensor** list — **Dispersivity** or **User defined**.

Select **Dispersivity** to specify the dispersion in terms of dispersivities (SI unit: m). Select an option from the **Dispersivity model** list: **Isotropic** (the default) or **Transverse isotropic** based on the properties of the porous media. For isotropic porous media, specify the longitudinal and transverse dispersivities. For transverse isotropic porous media, specify the longitudinal, horizontal transverse, and vertical transverse dispersivities.

For **User defined**, specify the dispersion components in terms of constants or expressions. Select **Isotropic**, **Diagonal**, **Symmetric**, or **Full** to enable the appropriate tensor components.

Unsaturated Porous Medium

Use this node to model the concentration of diluted species transported by a solvent (mobile fluid phase) through interstices in a solid porous medium. In addition to transport due to convection and diffusion, the node contains functionality to include species evolution through adsorption and dispersion.

Use this node to model the concentration of diluted species transported by a liquid (mobile fluid phase) in a partially filled solid porous medium. The interstices of the porous medium contains the liquid carrier phase and gas pockets. Apart from

convection and diffusion, the node contains functionality to include species evolution through adsorption, dispersion, and volatilization.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

The properties of each phase present are defined using the Liquid, the Gas, and the Porous Matrix subnodes respectively. The Unsaturated Porous Medium node supports material properties using a Porous Material node (described in the *COMSOL Multiphysics Reference Manual)*, where properties are defined per phase in a similar manner.

Add an Adsorption or a Dispersion subfeature to the **Unsaturated Porous Medium** to account for the corresponding transport mechanism.

Liquid

Use this node to specify the mass transfer in the mobile liquid solvent present in the pores of the Unsaturated Porous Medium.

MODEL INPUTS

The temperature model input is always available. By default, the **Temperature** model input is set to **Common model input**, and the temperature is controlled from Default Model Inputs under **Global Definitions** or by a locally defined Model Input. If a Heat Transfer interface is included in the component, it controls the temperature **Common model input**. Alternatively, the temperature field can be selected from another physics interface. All physics interfaces have their own tags (**Name**). For example, if a Heat Transfer in Fluids interface is included in the component, the **Temperature (ht)** option is available for T.

You can also select **User defined** from the **Temperature** model input in order to manually prescribe T.

SATURATION

Select **Saturation** or **Liquid volume fraction** from the list.

For **Saturation**, enter a value for s (dimensionless) between 0 and 1. The liquid volume fraction is then computed from the saturation and porosity as $\theta_l = \varepsilon_p s$.

For **Liquid volume fraction**, enter a value for θ_l (dimensionless) between 0 and the value of the porosity.

Select a **Liquid fraction time change**: **Liquid fraction constant in time** (the default), **Time change in liquid fraction**, or **Time change in pressure head**.

- For **Time change in fluid fraction**, enter $\mathrm{d}\theta/\mathrm{d}t$ (SI unit: $1/\mathrm{s}$).
- For **Time change in pressure head**, enter $\mathrm{d}H_\mathrm{p}/\mathrm{d}t$ (SI unit: m/s) and a **Specific moisture capacity** C_m (SI unit: $1/\mathrm{m}$). If a Darcy's Law interface is included in the component, the time change in pressure head solved for can be selected.

CONVECTION

If transport by convection is active, the velocity field of the solvent needs to be specified. For **User defined**, enter values or expressions for the velocity components in the input fields. This input option is always available. You can also select the velocity field solved for by a Fluid Flow interface added to the model component. These physics interfaces are available for selection in the **Velocity field** list.

DIFFUSION

Use this section to specify diffusion coefficients describing the diffusion of each species in the solvent liquid.

Use the **Source** list to select to pick up diffusion coefficients defined in a material or a Chemistry interface.

Select **Material**, and a **Liquid material** to use a diffusion coefficient in a material available in the model. User-defined property groups including a diffusion coefficient output property are available for selection in the **Liquid diffusion coefficient** list.

Select **Chemistry** to use a diffusion coefficient from a Chemistry interface added to model component. Diffusion coefficients are automatically defined when **Calculate transport properties** is selected on the interface level of a Chemistry interface. All defined diffusion coefficients are available for selection in the **Liquid diffusion coefficient** list.

For **User defined**, enter a value or expression for the **Liquid diffusion coefficient** $D_{\mathrm{L,i}}$ of each species in the corresponding input field.

In a porous medium the diffusivity is reduced due to the fact that the solid grains impede Brownian motion. Select an **Effective diffusivity model, liquid** to account for the reduced diffusivity in the liquid. The available models are **Millington and Quirk model**

(the default), **Bruggeman model**, **Tortuosity model**, or **No correction**. For **Tortuosity model**, enter a value for the tortuosity $\tau_{L,i}$ (dimensionless).

Note that multiple species, as well as Migration in Electric fields (described below) is only available for certain COMSOL Multiphysics add-on products. For details see: https://www.comsol.com/products/specifications/.

MIGRATION IN ELECTRIC FIELD

This section is available when the **Migration in electric field** check box is selected. From the **Electric potential** list, select the source of the electric field.

- For **User defined,** enter a value or expression for the **Electric potential** V. This input option is always available.
- Select the electric potential solved by an AC/DC-based interface that has added to the component.
- Select the electric potential defined or solved for by an Electrochemistry interface added to the component.

By default the **Mobility** is set to be calculated based on the species effective diffusivity and the temperature using the **Nernst-Einstein relation**. For **User defined**, select the appropriate scalar or tensor type — **Isotropic**, **Diagonal**, **Symmetric**, or **Full** — and type in the value or expression of the effective mobility $u_{me,i}$.

Enter the **Charge number** z_c for each species.

Gas

Use this node to specify the mass transfer in the gas phase present in the pores of the Unsaturated Porous Medium.

DIFFUSION

The settings for the diffusion of each species in the gas phase are identical to those in the Liquid subnode.

VOLATILIZATION

Enter a value for the volatilization isotherm $k_{G,c}$ (dimensionless) for each species.

Adsorption

Use this node to model adsorption of the (fluid phase) solute species onto the surface of the porous matrix. It is available as a subnode to the Porous Medium and the Unsaturated Porous Medium nodes.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

MATRIX PROPERTIES

The density of the porous media is needed when modeling adsorption to the surface of the porous matrix. Choose to input either the **Dry bulk density** ρ, or the **Solid phase density** ρ_s. The former is the density of the porous matrix including empty pores, while the latter corresponds to the density of the pure solid phase. The density can be defined from the domain material by selecting **From material**, or from a user defined expression. When a **Porous Material** is used on the selection, the density will be requested from a **Solid** subfeature. Several **Solid** features can be used to model a homogeneous mixture of several solid components.

ADSORPTION

Select an **Adsorption isotherm** — **Langmuir**, **Freundlich**, **Toth**, **BET**, or **User defined** to specify how to compute c_P, the amount of species sorbed to the solid phase (moles per unit dry weight of the solid):

- For **Langmuir**:

$$c_P = c_{P\max}\frac{K_L c}{1+K_L c} \quad , \quad K_P = \frac{\partial c_P}{\partial c} = \frac{K_L c_{P\max}}{(1+K_L c)^2}$$

  Enter a **Langmuir constant** $k_{L,c}$ (SI unit: m^3/mol) and an **Adsorption maximum** $c_{p,max,c}$ (SI unit: mol/kg).

- For **Freundlich**:

$$c_{\mathrm{P}} = K_{\mathrm{F}}\left(\frac{c}{c_{\mathrm{ref}}}\right)^{N} \quad , \quad K_P = \frac{\partial c_{\mathrm{P}}}{\partial c} = N\frac{c_{\mathrm{P}}}{c}$$

Enter a **Freundlich constant** $k_{\mathrm{F,c}}$ (SI unit: mol/kg), a **Freundlich exponent** $N_{\mathrm{F,c}}$ (dimensionless), and a **Reference concentration** $c_{\mathrm{ref,c}}$ (SI unit: $\mathrm{mol/m^3}$).

- For **Toth**:

$$c_{\mathrm{P}} = c_{\mathrm{Pmax}}\frac{b_{\mathrm{T}}c}{(1+(b_{\mathrm{T}}c)^{N_{\mathrm{T}}})^{1/N_{\mathrm{T}}}}$$

and

$$K_P = \frac{\partial c_{\mathrm{P}}}{\partial c} = c_{\mathrm{Pmax}}b_{\mathrm{T}}(1+(b_{\mathrm{T}}c)^{N_{\mathrm{T}}})^{-\left(1+\frac{1}{N_{\mathrm{T}}}\right)}$$

Enter a **Toth constant** $b_{\mathrm{T,c}}$ (SI unit: $\mathrm{m^3/mol}$), a **Toth exponent** $N_{\mathrm{T,c}}$ (dimensionless), and an **Adsorption maximum** $c_{\mathrm{p,max,c}}$ (SI unit: mol/kg).

- For **BET (Brunauer-Emmett-Teller)**:

$$c_{\mathrm{P}} = \frac{K_{\mathrm{B}}c_0 c}{(c_{\mathrm{S}}-c)\left(1+(K_{\mathrm{B}}-1)\frac{c}{c_{\mathrm{S}}}\right)}$$

and

$$K_P = \frac{\partial c_{\mathrm{P}}}{\partial c} = \frac{K_{\mathrm{B}}c_0 c_{\mathrm{S}}((K_{\mathrm{B}}-1)c^2+c_{\mathrm{S}}^2)}{(c-c_{\mathrm{S}})^2(c_{\mathrm{S}}+(K_{\mathrm{B}}-1)c)^2}$$

Enter a **BET constant** $K_{\mathrm{B,c}}$ (dimensionless), a **Monolayer adsorption capacity** $c_{0,\mathrm{c}}$ (SI unit: mol/kg), and an **Saturation concentration** $c_{\mathrm{S,c}}$ (SI unit: $\mathrm{mol/m^3}$).

- For **User defined** enter an **Adsorption isotherm** $c_{\mathrm{P,c}}$ (SI unit: mol/kg):

$$c_{\mathrm{P}} = f(c)$$

For more information, see Adsorption in the theory section.

FURTHER READING

See the theory chapter in the section Mass Balance Equation for Transport of Diluted Species in Porous Media.

Volatilization

This feature is available when the **Mass transfer in porous media** check box is selected on the **Settings** window for the physics interface.

Use this feature to model mass transfer at the boundary due to volatilization. The species dissolved in the liquid are assumed to be vaporized at the boundary, and transported into the surrounding bulk region due to convection and diffusion. The mass transfer at the boundary is defined as

$$-\mathbf{n} \cdot \mathbf{J}_c = -h_c(k_{G,c}c - c_{Gatm,c})$$

where h_c is the mass transfer coefficient, $k_{G,c}$ the volatilization coefficient, and $c_{Gatm,c}$ the concentration in the surrounding atmosphere.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

VOLATILIZATION

Enter a **Mass transfer coefficient** h_c defining the transfer into the surrounding media. This can be given by boundary layer theory. When assuming that no convective flow is present in the surrounding, the mass transfer coefficient can be defined from the gas diffusion coefficient D_{Gc} and the thickness of the diffusion layer d_s in the manner of

$$h_c = \frac{D_{Gc}}{d_s}$$

Also give the atmospheric concentration for each species, $c_{Gatm,c}$. The **Volatilization** coefficient $k_{G,c}$ for each species are taken from the adjacent Unsaturated Porous Medium domain.

Reactive Pellet Bed

Use this feature to model packed bed reactors with catalytic pellets. For details, see the section Theory for the Reactive Pellet Bed. By default, subnodes for Porous Media Diffusion, Reactions and Initial Values are added.

PELLET PROPERTIES

The default shape is spherical. Cylinders, flakes, and user-defined shapes can also be selected. A uniform pellet size or a discrete size distribution can be selected. Select a **Pellet size distribution** — **Uniform size** (the default), **Two sizes**, **Three sizes**, **Four sizes**, or **Five sizes** to select up to five different particle sizes.

Depending on the shape selection, equivalent radii or volumes and surface areas will be required as input. Enter a **Porosity** $\varepsilon_{\mathrm{pe}}$ (dimensionless) to specify the porosity of the pellet. If a size distribution is selected, the porosity and volume fraction of each size are required as input. The bed porosity is taken from the corresponding Porous Matrix feature, where the porosity can also be defined on the base of densities of bed and pellet.

Note that different chemical reactions can be specified for each pellet size if a distribution is specified.

PELLET-FLUID SURFACE

For the coupling of concentration between the pellet internals and the surrounding fluid, two **Coupling type** options are available:

- **Continuous concentration**, assuming that all resistance to mass transfer to/from the pellet is within the pellet and no resistance to pellet-fluid mass transfer is on the bulk fluid side. The concentration in the fluid will thus be equal to that in the pellet pore just at the pellet surface: $c_{\mathrm{pe},i} = c_i$. This constraint also automatically ensures flux continuity between the internal pellet domain and the free fluid domain through so-called reaction forces in the finite element formulation.
- **Film resistance (mass flux)**: The flux of mass across the pellet-fluid interface into the pellet is possibly rate determined on the bulk fluid side, by film resistance. The resistance is expressed in terms of a film mass transfer coefficient, h_{Di}, such that:

$$N_{i,\mathrm{inward}} = h_{D,i}(c_i - c_{\mathrm{pe},i})\,.$$

The **Film resistance (mass flux)** option computes the inward surface flux, h_{Di} is the mass transfer coefficient (SI unit: m/s) and is calculated with the default **Automatic** setting from a dimensionless **Sherwood number expression** or with **User defined** mass transfer coefficients.

The **Active specific surface area** (SI unit: m^{-1}) is required to couple the mass transfer between the pellets and the bed fluid. Select either the **Automatic** setting that calculates the specific surface area from the shape information given above. User defined is also available for explicit surface area specification.

The **Sherwood number expression** can be computed from three available expressions: **Frössling**, **Rosner**, and **Garner and Keey**. The Frössling equation is the default and probably the most commonly used for packed spheres. All of these are based on the dimensionless Reynolds, Re, and Schmidt, Sc, numbers, which are computed from **Density** and **Dynamic viscosity**. They can be taken **From material** or choose the **User defined** alternative. The expressions of density and dynamic viscosity from Chemistry could be available for both **Density** and **Dynamic viscosity.**

SURFACE SPECIES

In order to add surface species, click the **Add** button and enter the species name in the **Surface species** table. Added surface species are available inside all pellet types defined in the **Pellet Shape and Size** section, but not in the bulk fluid.

For each pellet type, specify the **Reactive specific surface area**, $S_{\mathrm{b,reac}}$ (SI unit: $1/\mathrm{m}$), corresponding to the surface area, per volume, available for surface reactions.

PELLET DISCRETIZATION

The extra dimension in the pellet needs to be discretized into elements. Select a **Distribution** — **Cubic root sequence** (the default), **Linear**, or **Square root sequence**. Enter the **Number of elements** N_{elem}.

CONSTRAINT SETTINGS

To display this section, click the **Show** button ( ) and select **Advanced Physics Options**. See the details about the different constraint settings in the section Constraint Reaction Terms in the *COMSOL Multiphysics Reference Manual*.

FURTHER READING

Theory for the Reactive Pellet Bed in the Theory section of this manual.

For an application using the Reactive Pellet Bed feature, see

- *A Multiscale 3D Packed Bed Reactor*: Application Library path **Chemical_Reaction_Engineering_Module/Reactors_with_Porous_Catalysts/packed_bed_reactor_3d**

  Web link: https://www.comsol.com/model/a-multiscale-3d-packed-bed-reactor-17019

Porous Media Diffusion

The Porous Media Diffusion subnode to the Reactive Pellet Bed is used to specify diffusion properties within the reactive pellets.

DOMAIN SELECTION

From the **Selection** list, choose the domains on which the mass transport by diffusion takes place.

Several diffusion nodes can be used to account for different diffusion processes in different porous parts for the modeling geometry.

DIFFUSION

Select **Diffusion model** — **Millington and Quirk model** (the default), **Bruggeman model**, **Tortuosity model**, or **User defined** to describe the effective correction of the diffusion coefficient in the pellet. In the case of the **Tortuosity model**, a value for the tortuosity τ_{pe} within the pellet is required. Use this section to specify diffusion models and diffusion coefficients inside the reactive pellet.

From the **Diffusion coefficient** list, select diffusion coefficient for different species. If a **User defined** diffusion model is selected, an **Effective diffusion coefficient** $D_{peff,c}$ (SI unit: m^2/s) is entered. The default value is $1 \cdot 10^{-9}$ m^2/s in both cases.

Diffusion coefficients calculated in Chemistry are available in the list when Chemistry is coupled to the Reactive Pellet Bed feature.

Reactions (Reactive Pellet Bed)

The Reactions subnode to the Reactive Pellet Bed is used to define reaction terms to the transport within the reactive pellets. The feature also defines the corresponding averaged heat sources to be applied to heat transport in the bulk fluid.

DOMAIN SELECTION

From the **Selection** list, choose the domains on which to define rate expression or expressions that govern source terms in the transport equations.

Several Reactions nodes can be used to account for different reactions in different parts for the modeling geometry.

REACTION RATES

Select a reaction rate (SI unit: mol/(m^3·s)) for species i from $R_{pe,i}$ list. Enter a reaction rate expression when User defined is selected from the list. Alternatively, if reaction rate expressions have been defined in a Chemistry interface, they can be chosen from the list.

- *Fine Chemical Production in a Plate Reactor*: Application Library path **Chemical_Reaction_Engineering_Module/ Reactors_with_Mass_and_Heat_Transfer/plate_reactor**

  Web link: https://www.comsol.com/model/fine-chemical-production-in-a-plate-reactor-8589

REACTING VOLUME

When specifying reaction rates for a species in the pellet, the specified reaction rate may have the basis of the pore volume, or the total volume. With the **Pore volume** selected, the reaction expression in mol/(m^3·s) will be multiplied by pellet's porosity ε_{pe}.

SURFACE REACTION RATES

The section is available when one or more surface species have been added in the **Surface Species** section of the Reactive Pellet Bed feature.

Specify the rate expression $R_{surf,i}$ (SI unit: mol/(m^2·s)) corresponding to the surface reaction rate of each volumetric species i participating in the surface reaction. Furthermore, specify the surface reaction rates for the participating surface species in the corresponding table.

If several pellet types have been defined, one set of surface reaction rates per pellet type can be defined. If reaction rate expressions have been defined in a Chemistry interface, they can be chosen from the list.

HEAT SOURCE

Specify the heat source originating from the heat of reaction of the chemical reactions inside the pellet. Both heat sources from reactions in the fluid, and heat sources resulting from surface reactions can be defined. When using several pellet types, heat sources for each type can be added.

The heat sources are most conveniently picked up from a Chemistry interface that defines the reaction rate and the heat of reactions. In that case, the heat source

expression can be selected from the list. Otherwise you can enter an expression in the text field.

The defined heat source can be used by a Heat Source feature in any of the heat transfer interfaces.

Species Source

In order to account for consumption or production of species in porous domains, the **Species Source** node adds source terms expressions S_i to the right-hand side of the species transport equations.

DOMAIN SELECTION

From the **Selection** list, choose the domains on which to define rate expression or expressions that govern the source term in the transport equations.

If there are several types of domains, with subsequent and different reactions occurring within them, it might be necessary to remove some domains from the selection. These are then defined in an additional **Species Source** node.

SPECIES SOURCE

Add a source term S_i (SI unit: mol/(m^3·s)) for each of the species solved for. Enter a value or expression in the field of the corresponding species.

Hygroscopic Swelling

The **Hygroscopic Swelling** multiphysics coupling node ( ) is used for moisture concentration coupling between the Solid Mechanics interface and either the Transport of Diluted Species or Transport of Diluted Species in Porous Media interfaces.

Hygroscopic swelling is an effect of internal strain caused by changes in moisture content. This volumetric strain can be written as

$$\varepsilon_{hs} = \beta_h M_m (c_{mo} - c_{mo,ref})$$

where β_h is the coefficient of hygroscopic swelling, M_m is the molar mass, c_{mo} is the moisture concentration, and $c_{mo,ref}$ is the strain-free reference concentration.

This feature requires a license of either the MEMS Module or the Structural Mechanics Module. The multiphysics feature will appear automatically if both the Transport of Diluted Species and the Solid Mechanics interfaces are added to the same component.

For the most current information about licensing, please see See https://www.comsol.com/products/specifications/.

FURTHER READING

More information about how to use hygroscopic swelling can be found in Hygroscopic Swelling Coupling section in the *Structural Mechanics Module User's Guide*.

More information about multiphysics coupling nodes can be found in the section The Multiphysics Branch in the *COMSOL Multiphysics Reference Manual*.

Fracture

Use this node to model mass transport along thin fractures in porous media. The node assumes that the transport in the tangential direction along the fracture is dominant, as a result of lower flow resistance.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

FRACTURE PROPERTIES

Specify a value for the **Fracture thickness** d_{fr}.

MATRIX PROPERTIES

Use the **Porous material** list to define a material specifying the matrix properties on the current selection. By default the **Boundary material** is used.

Specify the **Porosity,** ε_{p} (dimensionless) of the porous matrix. This is by default taken **From material**. Select **User defined** to instead enter a different value.

CONVECTION

Select an option from the **Velocity field** list to specify the convective velocity along the fracture. For a consistent model, use a Fracture Flow feature in a Darcy's Law interface to compute the fluid flow velocity in the fracture.

For **User defined**, enter values or expressions for the velocity components in the table shown.

	The settings for the **Diffusion** is the similar to the settings for the diffusion coefficients in the Fluid node. The **Dispersion** settings are identical to the ones in the Dispersion node.

The Transport of Diluted Species in Fractures Interface

The **Transport of Diluted Species in Fractures (dsf)** interface ( ), found under the **Chemical Species Transport** branch ( ), is used to model the transport of a solute species along thin porous fractures, taking into account diffusion, dispersion, convection, and chemical reactions. The fractures are defined by boundaries and the solute species is assumed to be present in a solvent.

The interface supports simulation of species transport along boundaries in 2D and 3D, and axisymmetric components in 2D. The dependent variable is the molar concentration, c. Modeling multiple species transport is possible, whereby the physics interface solves for the molar concentration, c_i, of each species i.

This interface is only available in a limited set of add-on products. For a detailed overview of which interfaces are available in each product, visit https://www.comsol.com/products/specifications/

SETTINGS

The **Label** is the default physics interface name.

The **Name** is used primarily as a scope prefix for variables defined by the physics interface. Refer to such physics interface variables in expressions using the pattern `<name>.<variable_name>`. In order to distinguish between variables belonging to different physics interfaces, the `name` string must be unique. Only letters, numbers, and underscores (_) are permitted in the **Name** field. The first character must be a letter.

The default **Name** (for the first physics interface in the model) is `dsf`.

BOUNDARY SELECTION

If model geometry includes boundaries that should not be included in the mass transfer simulation, remove those from the selection list.

TRANSPORT MECHANISMS

Mass transport due to diffusion is always included. Use the **Convection** check box, available under **Additional transport mechanisms**, to control whether to also include convective transport.

CONSISTENT STABILIZATION

To display this sections, click the **Show** button ( ) and select **Stabilization**. Use this section to control the application of the available consistent stabilization methods; **Streamline diffusion** and **Crosswind diffusion**.

- When the **Crosswind diffusion** check box is selected, a weak term that reduces spurious oscillations is added to the transport equation. The resulting equation system is always nonlinear. There are two options for the **Crosswind diffusion type**:
  - **Do Carmo and Galeão** — the default option. This type of crosswind diffusion reduces undershoots and overshoots to a minimum but can in rare cases give equation systems that are difficult to fully converge.
  - **Codina**. This option is less diffusive compared to the Do Carmo and Galeão option but can result in more undershoots and overshoots. It is also less effective for anisotropic meshes. The Codina option activates a text field for the **Lower gradient limit** g_{lim}. It defaults to `0.1[mol/m^3)/tds.helem`, where `tds.helem` is the local element size.
- For both consistent stabilization methods select an **Equation residual**. **Approximate residual** is the default and means that derivatives of the diffusion tensor components are neglected. This setting is usually accurate enough and is computationally faster. If required, select **Full residual** instead.

INCONSISTENT STABILIZATION

To display this section, click the **Show** button ( ) and select **Stabilization**. By default, the **Isotropic diffusion** check box is not selected, because this type of stabilization adds artificial diffusion and affects the accuracy of the original problem. However, this option can be used to get a good initial guess for under resolved problems.

DISCRETIZATION

To display all settings available in this section, click the **Show** button ( ) and select **Advanced Physics Options**.

The **Value type when using splitting of complex variables** setting should in most pure mass transfer problems be set to **Real**, which is the default. It makes sure that the dependent variable does not get affected by small imaginary contributions, which can occur, for example, when combining a Time Dependent or Stationary study with a frequency-domain study. For more information, see Splitting Complex-Valued Variables in the *COMSOL Multiphysics Reference Manual*.

DEPENDENT VARIABLES

The dependent variable name is **Concentration** c by default. A dependent variable name must be unique with respect to all other dependent variables in the component.

Add or remove species variables in the model and also change the names of the dependent variables that represent the species concentrations.

Enter the **Number of species**. Use the **Add concentration** (+) and **Remove concentration** ( ) buttons as needed.

FURTHER READING

- Mass Transport in Fractures in the theory section.
- Numerical Stabilization in the *COMSOL Multiphysics Reference Manual*.
- Domain, Boundary, and Pair Nodes for the Transport of Diluted Species Interface
- In the *COMSOL Multiphysics Reference Manual*, see Table 2-4 for links to common sections and Table 2-5 for common feature nodes. You can also search for information: press F1 to open the **Help** window or Ctrl+F1 to open the **Documentation** window.

Boundary, Edge, Point, and Pair Nodes for the Transport of Diluted Species in Fractures Interface

The Transport of Diluted Species Interface has the following boundary, edge, point, and pair nodes, listed in alphabetical order, available from the **Physics** ribbon toolbar (Windows users), **Physics** context menu (Mac or Linux users), or by right-clicking to access the context menu (all users).

- Adsorption
- Concentration
- Flux
- Fracture
- Inflow
- Initial Values
- No Flux
- Outflow
- Reactions
- Species Source

Adsorption

Use this node to model adsorption of the fluid phase species onto the porous media surface of the fracture.

MATRIX PROPERTIES

Use the **Porous material** list to define a material specifying the matrix properties on the current selection. By default the **Domain material** is used. The density of the porous media is needed when modeling adsorption to the surface of the porous matrix. By default **Density** ρ is set to from domain material.

ADSORPTION

Select an **Adsorption isotherm** — **Langmuir** (the default), **Freundlich**, **Toth**, **BET**, or **User defined** to specify how to compute c_P, the amount of species sorbed to the solid phase (moles per unit dry weight of the solid):

- For **Langmuir**:

$$c_P = c_{Pmax}\frac{K_L c}{1 + K_L c} \quad \frac{\partial c_P}{\partial c} = \frac{K_L c_{Pmax}}{(1 + K_L c)^2}$$

  Enter a **Langmuir constant** $k_{L,c}$ (SI unit: m^3/mol) and an **Adsorption maximum** $c_{p,max,c}$ (SI unit: mol/kg):

- For **Freundlich**:

$$c_P = K_F\left(\frac{c}{c_{ref}}\right)^N \quad \frac{\partial c_P}{\partial c} = N\frac{c_P}{c} \quad \text{Freundlich}$$

  Enter a **Freundlich constant** $k_{F,c}$ (SI unit: mol/kg), a **Freundlich exponent** $N_{F,c}$ (dimensionless), and a **Reference concentration** $c_{ref,c}$ (SI unit: mol/m^3).

- For **Toth**:

$$c_P = c_{Pmax}\frac{b_T c}{(1 + (b_T c)^{N_T})^{1/N_T}}$$

and

$$\frac{\partial c_P}{\partial c} = c_{Pmax} b_T (1 + (b_T c)^{N_T})^{-\left(1+\frac{1}{N_T}\right)}$$

Enter a **Toth constant** $b_{T,c}$ (SI unit: m^3/mol), a **Toth exponent** $N_{T,c}$ (dimensionless), and an **Adsorption maximum** $c_{p,max,c}$ (SI unit: mol/kg).

- For **BET (Brunauer-Emmett-Teller)**:

$$c_P = \frac{K_B c_0 c}{(c_S - c)\left(1 + (K_B - 1)\frac{c}{c_S}\right)}$$

and

$$\frac{K_B c_0 c_S ((K_B - 1)c^2 + c_S^2)}{(c - c_S)^2 (c_S + (K_B - 1)c)^2}$$

Enter a **BET constant** $K_{B,c}$ (dimensionless), a **Monolayer adsorption capacity** $c_{0,c}$ (SI unit: mol/kg), and an **Saturation concentration** $c_{S,c}$ (SI unit: mol/m^3).

- For **User defined**:

$$c_P = f(c)$$

Enter an adsorption isotherm $c_{P,c}$ (SI unit: mol/kg).

For more information, see Adsorption in the theory section.

FURTHER READING

See the theory chapter in the section Mass Balance Equation for Transport of Diluted Species in Porous Media.

Concentration

Use this node to specify the species concentration on a fracture boundary (applied in points in 2D and along edges in 3D). For example, a $c = c_0$ condition specifies the concentration of species c.

CONCENTRATION

Individually specify the concentration for each species. Select the check box for the **Species** to specify the concentration, and then enter a value or expression in the

corresponding field. To use another boundary condition for a specific species, click to clear the check box for the concentration of that species.

CONSTRAINT SETTINGS

To display this section, click the **Show** button ( ) and select **Advanced Physics Options**. You can find details about the different constraint settings in the section Constraint Reaction Terms in the *COMSOL Multiphysics Reference Manual*.

Flux

This node can be used to specify the species flux across a boundary of a porous fracture (applied in points in 2D and along edges in 3D). The flux of species c is defined as

$$\mathbf{n} \cdot (D_c \nabla c) = N_0$$

where N_0 is an arbitrary user-specified flux expression. For example, N_0 can represent a flux due to chemical reactions, or a phase change. A positive N_0 implies that the concentration inside the fracture increases.

INWARD FLUX

Specify the flux of each species individually. To use another boundary condition for a specific species, click to clear the check box for the mass fraction of that species.

Fracture

Use this node to model mass transport along thin fracture surfaces situated inside porous or solid material. The node assumes that the transport in the tangential direction of the fracture is dominant, as a result of lower flow resistance. Note that the fracture it self is modeled as porous.

MATRIX PROPERTIES

Use the **Porous material** list to define a material specifying the matrix properties on the current selection. By default the **Boundary material** is used.

Specify the **Porosity,** ε_p (dimensionless) of the porous matrix. This is by default taken **From material**. Select **User defined** to instead enter a different value.

CONVECTION

Select an option from the **Velocity field** list to specify the convective velocity along the fracture. For a consistent model, use The Fracture Flow Interface (available with the

Subsurface Flow Module and the Porous Media Flow Module) to compute the fluid flow velocity.

For **User defined**, enter values or expressions for the velocity components in the table shown.

The settings for the **Diffusion** is the similar to the settings for the diffusion coefficients in the Fluid node. The **Dispersion** settings are identical to the ones in the Dispersion node.

Inflow

Use this node to specify all species concentrations at a fracture inlet. The condition is applied in points in 2D and along edges in 3D.

If you want to specify the concentration of a subset of the partaking species, this can be done by using the Concentration node instead.

CONCENTRATION

For the concentration of each species $c_{0,c}$ (SI unit: mol/m^3), enter a value or expression.

BOUNDARY CONDITION TYPE

This section in the settings is only available for some products. Search for "Inflow" on the page: https://www.comsol.com/products/specifications/ for more details on availability.

The option **Concentration constraint** constrains the concentration values on the boundary by the use of pointwise constraints. The other option, **Flux (Danckwerts)** can be more stable and fast to solve when high reaction rates are anticipated in the vicinity of the inlet. Oscillations on the solutions can also be avoided in such cases. The latter condition uses a flux boundary condition based on the velocity across the boundary and the concentration values. See further details in the theory section.

CONSTRAINT SETTINGS

To display this section, click the **Show** button ( ) and select **Advanced Physics Options**. You can find details about the different constraint settings in the section Constraint Reaction Terms in the *COMSOL Multiphysics Reference Manual*.

FURTHER READING

See the theory chapter in the section Danckwerts Inflow Boundary Condition.

No Flux

This node can be used to specify that the species flux across a boundary of a porous fracture is zero. The condition is applied in points in 2D and along edges in 3D.

Outflow

Set this condition at fracture outlets where species are transported out of the model domain by fluid motion. The condition is applied in points in 2D and along edges in 3D. It is assumed that convection is the dominating transport mechanism across outflow boundaries, and therefore that diffusive transport can be ignored, that is:

$$\mathbf{n} \cdot (-D_e \nabla c) = 0$$

Reactions

Use the **Reactions** node to account for the consumption or production of species through chemical reactions in the fracture. Define the rate expressions as required.

BOUNDARY SELECTION

From the **Selection** list, choose the boundaries on which to define rate expression or expressions that govern the source term in the transport equations.

Several reaction nodes can be used to account for different reactions in different parts of the fracture.

REACTION RATES

Add a rate expression R_i for species i. Enter a value or expression in the field. Note that if you have the *Chemistry* interface available, provided with the *Chemical Reaction Engineering Module*, the reaction rate expressions can be automatically generated and picked up using the drop-down menu.

REACTING VOLUME

When specifying reaction rates for a species in a fracture, the specified reaction rate may have the basis of the pore volume of the fracture, or the total volume.

- For **Total volume**, the reaction expressions in are specified per unit volume of the fracture. The reaction expressions will be multiplied by the fracture thickness d_{fr}.
- For **Pore volume**, the reaction expressions in mol/(m^3·s) are specified per unit volume of total pore space in the fracture. The reaction expressions will be multiplied by the fracture thickness d_{fr} and the fracture porosity, ε_{p}.

Species Source

In order to account for consumption or production of species in a fracture, the **Species Source** node adds source terms expressions S_i to the right-hand side of the species transport equations.

BOUNDARY SELECTION

From the **Selection** list, choose the boundaries on which to define expressions that govern the source term in the transport equations.

If there are several different parts of the fracture, with subsequent and different sources occurring within them, it might be necessary to remove some boundaries from the selection. The sources in these can then be defined using an additional **Species Source** node.

SPECIES SOURCE

Add a source term S_i for each of the species solved for. Enter a value or expression in the field of the corresponding species.

The Transport of Concentrated Species Interface

The **Transport of Concentrated Species (tcs)** interface ( ), found under the **Chemical Species Transport** branch ( ) when adding a physics interface, is used to study gaseous and liquid mixtures where the species concentrations are of the same order of magnitude and none of the species can be identified as a solvent. In this case, properties of the mixture depend on the composition, and the molecular and ionic interactions between all species need to be considered. The physics interface includes models for multicomponent diffusion, where the diffusive driving force of each species depends on the mixture composition, temperature, and pressure.

The physics interface solves for the mass fractions of all participating species. Transport through convection, diffusion, and migration in an electric field can be included.

It supports simulations of transport by convection, migration, and diffusion in 1D, 2D, and 3D as well as for axisymmetric components in 1D and 2D. The physics interface defines the equations for the species mass fractions, including a diffusion model (Mixture-averaged, Maxwell–Stefan, or Fick's law).

The available transport mechanisms and diffusion models differs between various COMSOL products (see https://www.comsol.com/products/specifications/).

Some examples of what can be studied with this physics interface include:

- The evolution of a chemical species transported by convection and diffusion.
- The migration in an electric field in the case of ionic species, in mixtures and solutions that cannot be deemed as being diluted.
- Concentrated solutions or gas mixtures, where the concentration of all participating species are of the same order of magnitude, and their molecular and ionic interaction with each other therefore must be considered. This implies that the diffusive transport of a single species is dependent on the mixture composition, and possibly on the temperature, the electric potential, the pressure, or any combination.

When this physics interface is added, the following default nodes are also added in the **Model Builder** — **Transport Properties**, **No Flux**, and **Initial Values**. Then, from the **Physics** toolbar, add other nodes that implement, for example, boundary conditions and reactions. You can also right-click **Transport of Concentrated Species** to select physics features from the context menu.

SETTINGS

The **Label** is the default physics interface name.

The **Name** is used primarily as a scope prefix for variables defined by the physics interface. Refer to such physics interface variables in expressions using the pattern `<name>.<variable_name>`. In order to distinguish between variables belonging to different physics interfaces, the `name` string must be unique. Only letters, numbers, and underscores (_) are permitted in the **Name** field. The first character must be a letter.

The default **Name** (for the first physics interface in the model) is `tcs`.

EQUATION

The basic equation for the conservation of mass of a species i is:

$$\frac{\partial}{\partial t}(\rho\omega_i) + \nabla \cdot (\rho\omega_i \mathbf{u}) = -\nabla \cdot \mathbf{j}_i + R_i \quad (3\text{-}121)$$

Using the continuity equation, the sum of all species equations, the equation can be re-cast in its non-conservative form:

$$\rho\frac{\partial}{\partial t}(\omega_i) + \rho(\mathbf{u} \cdot \nabla)\omega_i = -\nabla \cdot \mathbf{j}_i + R_i \quad (3\text{-}122)$$

The form of the equation is the one which is used the Transport of Concentrated Species interface. The equation displayed in the interface changes depending on the active transport mechanisms, the selected diffusion model, and the type of reactions modeled.

TRANSPORT MECHANISMS

The Transport of Concentrated Species interface always accounts for transport due to diffusion.

The available diffusion models and the additional transport mechanisms differs between various COMSOL products (see https://www.comsol.com/products/specifications/).

Diffusion Model

- The **Maxwell–Stefan** option employs the most detailed diffusion model, but is also the most computationally expensive. The model is intended for diffusion dominated models, and requires that the multicomponent Maxwell–Stefan diffusivities of all component pairs are known. No stabilization is available when selecting this model.

- The **Mixture-averaged** option is less computationally expensive than the Maxwell–Stefan model. It is a simpler model that can be used when variations in the partial pressures and temperature can be assumed to not affect the multicomponent diffusion. The model includes stabilization but requires the multicomponent Maxwell–Stefan diffusivities of all component pairs.
- The **Fick's law** model is a general model that should be used when the diffusion is assumed Fickian, or when no multicomponent diffusivities are available. Also, when molecular diffusion is not the dominating transport mechanism and a robust but low order model is wanted, the Fick's law options should be used. The model includes stabilization.

Additional Transport Mechanisms

Under **Additional transport mechanisms**, click to select or clear any combination of check boxes as needed.

Migration in Electric Field

Select the **Migration in electric field** check box to activate migration of ionic species due to an electric field. The resulting migration term is part of the relative mass flux vector.

Mass Transport in Porous Media

The **Mass transport in porous media** check box activates functionality specific to species transport in porous media. When selected the following features are enabled:

- Porous Media Transport Properties
- Porous Electrode Coupling

Knudsen Diffusion

For **Mixture-averaged** and **Fick's law**, it is possible to include **Knudsen diffusion**. This mechanism accounts for species collisions with the surrounding media, for example, the pore walls the species pass through. It is also an important component when setting up a Dusty gas model.

Maxwell–Stefan Diffusion Model

When using the **Maxwell–Stefan** diffusion model the relative mass flux vector is

$$\mathbf{j}_i = -\rho\omega_i \sum_{k=1}^{Q} \tilde{D}_{ik}\mathbf{d}_k - \frac{D_i^T}{T}\nabla T$$

where $\tilde{D}_{ik}$ (SI unit: m^2/s) are the multicomponent Fick diffusivities, $\mathbf{d}_k$ (SI unit: $1/m$) is the diffusional driving force, T (SI unit: K) is the temperature, and D_i^T (SI unit: $kg/(m \cdot s)$) is the thermal diffusion coefficient.

The diffusional driving force is defined as

$$\mathbf{d}_k = \nabla x_k + \frac{1}{p}\left[(x_k - \omega_k)\nabla p - \rho\omega_k \mathbf{g}_k + \omega_k \sum_{l=1}^{Q} \rho\omega_l \mathbf{g}_l\right] \quad (3\text{-}123)$$

where $\mathbf{g}_k$ is an external force (per unit mass) acting on species k. In the case of an ionic species, the external force due to the electric field, which is added by selecting the **Migration in electric field** check box, is

$$\mathbf{g}_k = -\frac{z_k F}{M_k}\nabla\phi \quad (3\text{-}124)$$

where z_k is the species charge number, F (SI unit: A·s/mol) is Faraday's constant and ϕ (SI unit: V) is the electric potential.

Mixture-Averaged Diffusion Model

When using the **Mixture-averaged** diffusion model, the diffusive flux is formulated in terms of a mixture-averaged diffusion coefficient representing the diffusion of each species into the resulting mixture. The diffusion coefficient is based on the multicomponent Maxwell–Stefan diffusivities D_{ik}. The **Mixture-averaged** diffusion model is computationally less expensive, and significantly more robust than the Maxwell–Stefan Diffusion Model, but constitutes an approximation of the multicomponent flux. For information on the flux formulation in this case see Multicomponent Diffusion: Mixture-Averaged Approximation.

Fick's Law Diffusion Model

When using the **Fick's law** diffusion model, the diffusive flux is formulated in terms of a Fickian diffusion coefficient. The **Fick's law** diffusion model is computationally less expensive and significantly more robust than the Maxwell–Stefan Diffusion Model, but constitutes an approximation of the multicomponent flux. For information on the flux formulation in this case see Multispecies Diffusion: Fick's Law Approximation.

SPECIES

Select the species that this physics interface solves for using the mass constraint in Equation 3-125 (that is, its value comes from the fact that the sum of all mass fractions must equal 1). In the **From mass constraint** list, select the preferred species. To

minimize the impact of any numerical and model introduced errors, use the species with the highest concentration. By default, the first species is used.

$$\omega_1 = 1 - \sum_{i=2}^{Q} \omega_i \tag{3-125}$$

CONSISTENT AND INCONSISTENT STABILIZATION

To display this section, click the **Show** button ( ) and select **Stabilization**.

- There are two consistent stabilization methods available when using the Mixture-Averaged Diffusion Model or Fick's Law Diffusion Model — **Streamline diffusion** and **Crosswind diffusion**. Both are active by default.

  The **Residual** setting applies to both the consistent stabilization methods. **Approximate residual** is the default setting and it means that derivatives of the diffusion tensor components are neglected. This setting is usually accurate enough and computationally faster. If required, select **Full residual** instead.

- There is one inconsistent stabilization method, **Isotropic diffusion**, which is available when using the Mixture-Averaged Diffusion Model or Fick's Law Diffusion Model.

ADVANCED SETTINGS

To display this section, click the **Show** button ( ) and select **Advanced Physics Options**. Normally these settings do not need to be changed.

Regularization

From the **Regularization** list, select **On** (the default) or **Off**. When turned **On**, regularized mass fractions are calculated such that

$$0 \le w_{i,\,\mathrm{reg}} \le 1$$

Regularized mass fractions are used for the calculation of composition-dependent material properties, such as the density.

Diffusion

The **Diffusion** settings are available for the approximate diffusion models Mixture-averaged and Fick's law.

When the **Mixture diffusion correction** is enabled, a flux correction is added to ensure that the net diffusive flux is zero. This typically also mean that the solution becomes less sensitive to the species selected to be computed from the mass constraint in the

Species section. More information on this correction is available in the theory section Multicomponent Diffusion: Mixture-Averaged Approximation.

The **Diffusion flux type** list controls the whether the molecular flux is assumed proportional to the mole fraction or the mass fraction. See Multicomponent Diffusion: Mixture-Averaged Approximation or Multispecies Diffusion: Fick's Law Approximation for information on the diffusive flux formulation.

Pseudo Time Stepping

The **Use pseudo time stepping for stationary equation form** option adds pseudo time derivatives to the equation when the **Stationary** equation form is used in order to speed up convergence. When selected, a CFL number expression should also be defined. For the default **Automatic** option, the local CFL number (from the Courant–Friedrichs–Lewy condition) is determined by a PID regulator. For more information, see Pseudo Time Stepping for Mass Transport.

DISCRETIZATION

To display all settings available in this section, click the **Show** button ( ) and select **Advanced Physics Options**.

For more information about these settings, see the *Discretization* section under The Transport of Diluted Species Interface.

In the *COMSOL Multiphysics Reference Manual* see Table 2-4 for links to common sections and Table 2-5 to common feature nodes. You can also search for information: press F1 to open the **Help** window or Ctrl+F1 to open the **Documentation** window.

- Domain, Boundary, and Pair Nodes for the Transport of Concentrated Species Interface
- Theory for the Transport of Concentrated Species Interface

- *Species Transport in the Gas Diffusion Layers of a PEM*: Application Library path **Fuel_Cell_and_Electrolyzer_Module/Fuel_Cells/pem_gdl_species_transport_2d**

  Web link: https://www.comsol.com/model/species-transport-in-the-gas-diffusion-layers-of-a-pem-260

DEPENDENT VARIABLES

Add or remove species in the model and also change the names of the dependent variables that represent the species concentrations.

Specify the **Number of species**. There must be at least two species. To add a single species, click the **Add concentration** button ( ) under the table. To remove a species, select it in the list and click the **Remove concentration** button ( ) under the table. Edit the names of the species directly in the table.

The species are dependent variables, and their names must be unique with respect to all other dependent variables in the component.

Adding a Chemical Species Transport Interface and Specifying the Number of Species

Domain, Boundary, and Pair Nodes for the Transport of Concentrated Species Interface

The Transport of Concentrated Species Interface has these domain, boundary, and pair nodes, listed in alphabetical order, available from the **Physics** ribbon toolbar (Windows users), **Physics** context menu (Mac or Linux users), or right-click to access the context menu (all users).

In general, to add a node, go to the **Physics** toolbar, no matter what operating system you are using. Subnodes are available by clicking the parent node and selecting it from the **Attributes** menu.

In the *COMSOL Multiphysics Reference Manual* see Table 2-4 for links to common sections and Table 2-5 to common feature nodes. You can also search for information: press F1 to open the **Help** window or Ctrl+F1 to open the **Documentation** window.

For axisymmetric components, COMSOL Multiphysics takes the axial symmetry boundaries (at $r = 0$) into account and automatically adds an **Axial Symmetry** node to the component that is valid on the axial symmetry boundaries only.

These nodes are described in this section or as indicated:

- Electrode Surface Coupling
- Equilibrium Reaction
- Flux
- Flux Discontinuity
- Inflow
- Initial Values
- Mass Fraction
- No Flux
- Open Boundary
- Outflow
- Pellet Transport Properties
- Porous Media Transport Properties
- Reaction
- Reaction Sources
- Reaction Sources (Reactive Pellet Bed)
- Reactive Pellet Bed
- Surface Equilibrium Reaction
- Symmetry
- Thin Impermeable Barrier[1]
- Turbulent Mixing
- Transport Properties

Some features require certain add-on modules. See details https://www.comsol.com/products/specifications/

[1] The node is described for the Transport of Diluted Species interface.

Transport Properties

The **Transport Properties** is the main node used to model mass transfer in a fluid mixture with the Transport of Concentrates species interface. The node adds the equations governing the mass fractions of all present species, and provides inputs for the transport mechanisms and for the material properties of the fluid mixture.

The settings in this node are dependent on the check boxes selected under Transport Mechanisms in the Settings window of the Transport of Concentrated Species interface.

The Turbulent Mixing subnode is available from the context menu as well as from the **Physics** toolbar, **Attributes** menu.

The options available in this feature differs between COMSOL products. (See https://www.comsol.com/products/specifications/).

MODEL INPUTS

Specify the temperature and pressure to be used in the physics interface. The temperature model input is used when calculating the density from the ideal gas law, but also when thermal diffusion is accounted for by supplying thermal diffusion coefficients. The pressure model input is used in the diffusional driving force in Equation 3-123 (that is, when a Maxwell–Stefan Diffusion Model is used) and when calculating the density from the ideal gas law.

Temperature

Select the source of the **Temperature** field T:

- Select **User defined** to enter a value or an expression for the temperature (SI unit: K). This input is always available.
- If required, select a temperature defined by a Heat Transfer interface present in the model (if any). For example, select **Temperature (ht)** to use the temperature defined by the Heat Transfer in Fluids interface with the `ht` name.

Absolute Pressure

Select the source of the **Absolute pressure** p:

- Select **User defined** to enter a value or an expression for the absolute pressure (SI unit: Pa). This input is always available.
- In addition, select a pressure defined by a Fluid Flow interface present in the model (if any). For example, select **Absolute pressure (spf)** to use the pressure defined in a Laminar Flow interface with `spf` as the Name.

DENSITY

Define the density of the mixture and the molar masses of the participating species.

Mixture Density

Select a way to define the density from the **Mixture density** list — **Ideal gas** or **User defined**:

- For **Ideal gas**, the density is computed from the ideal gas law in the manner of:

$$\rho = \frac{pM}{R_g T}$$

Here M is the mean molar mass of the mixture and R_g is the universal gas constant. The absolute pressure, p, and temperature, T, used corresponds to the ones defined in the Model Inputs section.

- For **User defined** enter a value or expression for the **Mixture density** ρ.

Molar Mass

Enter a value or expression for the **Molar mass** M_w for each species. The default value is 0.032 kg/mol, which is the molar mass of O_2 gas.

CONVECTION

Select the source of the **Velocity field** $\mathbf{u}$:

- Select **User defined** to enter manually defined values or expressions for the velocity components. This input is always available.
- Select a velocity field defined by a Fluid Flow interface present in the model (if any). For example, select **Velocity field (spf)** to use the velocity field defined by the **Fluid Properties** node `fp1` in a Single-Phase Flow, Laminar Flow interface with `spf` as the Name.

DIFFUSION

Specify the molecular and thermal diffusivities of the present species based on the selected **Diffusion model**.

When using a Maxwell–Stefan Diffusion Model or a Mixture-Averaged Diffusion Model, select the **Binary diffusion input type** (Table or Matrix) and specify the **Maxwell–Stefan diffusivities** in the table or matrix, then enter the **Thermal diffusion coefficients** D_w^T.

When using a Fick's Law Diffusion Model, specify the **Diffusion coefficient** D_w^F and the **Thermal diffusion coefficients** D_w^T for each of the species.

Maxwell–Stefan Diffusivity Matrix

Using a Maxwell–Stefan Diffusion Model or a Mixture-Averaged Diffusion Model, the **Maxwell–Stefan diffusivity matrix** D_{ik} (SI unit: m^2/s) can be specified by a table or matrix. For a simulation involving Q species the Maxwell–Stefan diffusivity matrix is a Q-by-Q symmetric matrix, where the diagonal components are 1. Enter values for the upper triangular components, D_{ij}, which describe the interdiffusion between species i and j. For the table input type, only upper triangular components (D_{ij}) are listed. The

name of species pair consists of species in the first and second column. For the matrix input type, the numbering of the species corresponds to the order, from top to bottom, used for all the input fields for species properties (see for example the molar mass fields in the Density section). The Maxwell–Stefan diffusivity matrix is used to compute the multicomponent Fick diffusivities as described in Multicomponent Diffusivities.

Diffusion Coefficient

Using a Fick's Law Diffusion Model, the diffusion is by default assumed to be isotropic and governed by one **Diffusion coefficient** D_w^F (SI unit: m^2/s) for each species. To allow for a general representation, it is also possible to use diffusion matrices (diagonal, symmetric, or anisotropic).

Thermal Diffusion Coefficient

To model thermal diffusion, prescribe the **Thermal diffusion coefficients** D_i^T (SI unit: kg/(m·s)), by entering one thermal diffusion coefficient for each species in the corresponding field. In a multicomponent mixture, the sum of the thermal diffusion coefficients is zero. The default value for all thermal diffusion coefficients is 0.

Specify the molecular and thermal diffusivities of the present species based on the selected **Diffusion model**.

KNUDSEN DIFFUSION

The Knudsen diffusion transport mechanism accounts for the interaction of the species with the surroundings (interspecies collisions excluded) — for example, the pore wall when a species passes through porous media.

Depending on which **Diffusion model** is selected, either the **Fick's law** or the **Mixture-averaged** diffusion coefficient D_i^M is corrected with the **Knudsen diffusion** coefficient D_i^K in the following way

$$D_i^{MK} = \left(\frac{1}{D_i^M} + \frac{1}{D_i^K}\right)^{-1}$$

For gases, the **Kinetic gas theory** is often valid and requires the **Mean path length** λ_{path} (SI unit: m). Typically, for transport in porous media, the pore diameter can be entered here. For other cases, choose **User defined**.

MIGRATION IN ELECTRIC FIELD

This section is available when the **Migration in electric field** check box is selected for the Transport of Concentrated Species interface.

Electric Potential

- Select **User defined** to enter a value or expression for the electric potential. This input is always available.
- If required, select an electric potential defined by an AC/DC interface that is present in the model (if any). For example, select **Electric potential (ec)** to use the electric field defined by the Current Conservation node `cucn1` in an Electric Currents interface `ec`.

Settings for the mobilities are used for the **Mixture-averaged** and **Fick's law** transport models. By default the mobility is set to be calculated based on the species diffusivities and the temperature using the **Nernst-Einstein relation**. To manually specify the mobilities, select **User defined** for the mobility $u_{\mathrm{m,c}}$ (SI unit: s·mol/kg) and enter one value for each species.

Enter the **Charge number** z_{c} (dimensionless, but requires a plus or minus sign) for each species.

The temperature (if you are using mobilities based on the Nernst-Einstein relation) is taken from the **Model Inputs** section.

Porous Media Transport Properties

The **Porous Media Transport Properties** node is used to model mass transfer in porous media using the Transport of Concentrated Species interface. The node adds the equations governing the mass fractions of all present species, and provides inputs for the transport mechanisms and for the material properties of the fluid mixture.

The settings in this node are dependent on the check boxes selected under Transport Mechanisms in the Settings window of the Transport of Concentrated Species interface.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

MODEL INPUTS

Specify the temperature and pressure to be used in the physics interface. The temperature model input is used when calculating the density from the ideal gas law, but also when thermal diffusion is accounted for by supplying thermal diffusion coefficients. The pressure model input is used in the diffusional driving force in Equation 3-123 (that is, when a Maxwell–Stefan Diffusion Model is used) and when calculating the density from the ideal gas law.

Temperature

Select the source of the **Temperature** field T:

- Select **User defined** to enter a value or an expression for the temperature (SI unit: K). This input is always available.
- If required, select a temperature defined by a Heat Transfer interface present in the model (if any). For example, select **Temperature (ht)** to use the temperature defined by the Heat Transfer in Fluids interface with the `ht` name.

Absolute Pressure

Select the source of the **Absolute pressure** p:

- Select **User defined** to enter a value or an expression for the absolute pressure (SI unit: Pa). This input is always available.
- In addition, select a pressure defined by a Fluid Flow interface present in the model (if any). For example, select **Absolute pressure (spf)** to use the pressure defined in a Laminar Flow interface with `spf` as the name.

MATRIX PROPERTIES

The default selection for **Porosity** is **From material**. In order to use a porosity defined in a material, specify the material using the **Porous material** list, and select **From material** from the **Porosity** list.

Select **From pellet bed densities** to compute the porosity using the (dry bulk) **Bed density** ρ_b and the (single phase) **Pellet density** ρ_{pe} (for example, when there is a reactive pellet bed in the same domain). The porosity is then defined from

$$\varepsilon_p = 1 - \frac{\rho_b}{\rho_{pe}}$$

For **User defined**, enter a value or expression for the **Porosity,** ε_p (dimensionless), of the porous media.

DENSITY

Use this section to define the mixture density, and to specify the molar masses of the participating species.

Mixture Density

Select a way to define the density from the **Mixture density** list — **Ideal gas** or **User defined**:

- For **Ideal gas**, the density is computed from the ideal gas law in the manner of:

$$\rho = \frac{pM}{R_g T}$$

  Here M is the mean molar mass of the mixture and R_g is the universal gas constant. The absolute pressure, p, and temperature, T, used corresponds to the ones defined in the Model Inputs section.

- For **User defined** enter a value or expression for the **Mixture density** ρ.

Molar Mass

Enter a value or expression for the **Molar mass** M_w for each species. The default value is 0.032 kg/mol, which is the molar mass of O_2 gas.

CONVECTION

Select the source of the **Velocity field** $\mathbf{u}$:

- Select **User defined** to enter values or expressions for the velocity components. This input is always available.
- Select a velocity field defined by a Fluid Flow interface present in the model (if any). For example, select **Velocity field (spf)** to use the velocity field defined by the **Fluid Properties** node `fp1` in a Single-Phase Flow, Laminar Flow interface with `spf` as the Name.

DIFFUSION

Specify the species molecular and thermal diffusivities in nonporous media in the manner described for the Transport Properties node.

To account for the effect of porosity in the diffusivities, select an **Effective diffusivity model** — **Millington and Quirk model**, **Bruggeman model**, **Tortuosity model**, or **No correction**. Using one of the first four models, the effective transport factor, f_e, is defined from the porosity and the fluid tortuosity factor in the manner of:

$$f_e = \frac{\varepsilon_p}{\tau_F} \tag{3-126}$$

For **No correction**, the effective transport factor is set to one.

- For the **Millington and Quirk model**, the effective transport factor is $\tau_F = \varepsilon_p^{-1/3}$.
- For the **Bruggeman model**, the effective transport factor is $\tau_F = \varepsilon_p^{-1/2}$.
- For the **Tortuosity model**, specify the tortuosity factor is τ_F.

The species diffusivities and mobilities are automatically adjusted for porous media transport using the effective transport factor.

MIGRATION IN ELECTRIC FIELD

This section is available when the **Migration in electric field** check box is selected in the Transport Mechanisms section of the interface, select the source of the **Electric potential** V:

- Select **User defined** to enter a value or expression for the electric potential. This input is always available.
- If required, select an electric potential defined by an AC/DC interface that is present in the model (if any). For example, select **Electric potential (ec)** to use the electric field defined by the Current Conservation node `cucn1` in an Electric Currents interface `ec`.

Settings for the mobilities are needed for the **Mixture-averaged** and **Fick's law** diffusion models. By default the mobility is set to be calculated based on the species diffusivities (adjusted by the **Effective diffusivity model** in the **Diffusion** section) using the **Nernst-Einstein relation**. To manually specify the mobilities, select **User defined** for the mobility $u_{m,w}$ (SI unit: s·mol/kg) and enter one value for each species.

Enter the **Charge number** z_c (dimensionless, but requires a plus or minus sign) for each species.

The temperature (if you are using mobilities based or the Nernst-Einstein relation) is taken from the **Model Inputs** section.

Reactive Pellet Bed

Use this feature to model packed bed reactors with catalytic pellets in porous media. For details, see the section Theory for the Reactive Pellet Bed. By default, the

following subnodes are added; Pellet Transport Properties, Reaction Sources (Reactive Pellet Bed), and Initial Values.

PELLET PROPERTIES

The default shape is spherical. Cylinders, flakes, and user-defined shapes can also be selected. A uniform pellet size or a discrete size distribution can be selected. Select a **Pellet size distribution** — **Uniform size** (the default), **Two sizes**, **Three sizes**, **Four sizes**, or **Five sizes** to select up to five different particle sizes.

Depending on the shape selection, equivalent radii or volumes and surface areas will be required as input. Enter a **Porosity** $\varepsilon_{\mathrm{pe}}$ (dimensionless) to specify the porosity of the pellet. Note that the bed porosity is taken from the corresponding Porous Media Transport Properties feature, where the porosity can also be defined on the base of densities of bed and pellet. Select **Pellet temperature** T_{pe} — **From physics** (the default). The temperature is required to calculate the density to solve the pressure inside the pellet. If a size distribution is selected, the porosity, volume fraction and temperature of each size are required as input. The temperature for all pellets are supposed to be the same when selecting **All pellets** from list of **Individual or all pellets**.

Note that if a distribution is specified, the **Fluid density**, **Dynamic viscosity** and **Permeability** in subnode Pellet Transport Properties need to be specified for each pellet, and the same to **Reaction Rates** in subnode Reaction Sources.

PELLET-FLUID SURFACE

For the coupling of concentration between the pellet internals and the surrounding fluid, two **Coupling type** options are available:

- **Mass fraction constraint**, assuming that all resistance to mass transfer to/from the pellet is within the pellet and no resistance to pellet-fluid mass transfer is on the bulk fluid side. The mass fraction in the fluid will thus be equal to that in the pellet pore just at the pellet surface: $\omega_{\mathrm{pe},i} = \omega_i$ and $p_{\mathrm{pe}} = p_A$ or $\rho_{\mathrm{pe},i}\,\omega_{\mathrm{pe},i} = \rho_i\,\omega_i$. This constraint also automatically ensures flux continuity between the internal pellet domain and the free fluid domain through so-called reaction forces in the finite element formulation.
- **Film resistance (mass flux)**: The flux of mass across the pellet-fluid interface into the pellet is possibly rate-determined on the bulk fluid side, by film resistance. The resistance is expressed in terms of a film mass transfer coefficient, h_{Di}, such that:

$$N_{i,\mathrm{inward}} = h_{D,i}(c_i - c_{\mathrm{pe},i})\,.$$

The **Film resistance (mass flux)** option computes the inward surface flux, h_{Di} is the mass transfer coefficient (SI unit: m/s) and is calculated with the default **Automatic** setting from a dimensionless **Sherwood number expression** or with **User defined** mass transfer coefficients.

The **Active specific surface area** (SI unit: m^{-1}) is required to couple the mass transfer between the pellets and the bed fluid. Select either the **Automatic** setting that calculates the specific surface area from the shape information given above. User defined is also available for explicit surface area specification.

The **Sherwood number expression** can be computed from three available expressions: **Frössling**, **Rosner**, and **Garner and Keey**. The Frössling equation is the default and probably the most commonly used for packed spheres. All of these are based on the dimensionless Reynolds, Re, and Schmidt, Sc, numbers, which are computed from **Density** and **Dynamic viscosity**. The Density can be taken from **From material, Density (tcs)** (from physics) and **User defined**, while Dynamic viscosity can be taken either **From material** or choose the **User defined** alternative. The expressions of density and dynamic viscosity from Chemistry could be available for both **Density** and **Dynamic viscosity.**

PELLET DISCRETIZATION

The extra dimension in the pellet needs to be discretized into elements. Select a **Distribution** — **Cubic root sequence** (the default), **Linear**, or **Square root sequence**. Enter the **Number of elements** N_{elem}.

CONSTRAINT SETTINGS

To display this section, click the **Show** button ( ) and select **Advanced Physics Options**. See the details about the different constraint settings in the section Constraint Reaction Terms in the *COMSOL Multiphysics Reference Manual*.

Pellet Transport Properties

The Pellet Transport Properties subnode to the Reactive Pellet Bed is used to specify fluid flow properties and diffusion coefficients within the reactive pellets.

DOMAIN SELECTION

From the **Selection** list, choose the domains on which the fluid flows through.

Several transport properties nodes can be added for different fluids in different porous parts for the modeling geometry.

FLUID AND MATRIX PROPERTIES

Select density, dynamic viscosity and permeability from the **Fluid density**, **Dynamic viscosity**, and **Permeability** lists, respectively. For both **Fluid density** and **Dynamic viscosity**, the density and viscosity from Chemistry could be available in these lists. If there are more than two different pellets, the fluid properties can be set to the same for all pellets by selecting **All pellets** from the **Individual or all pellets** list, or set for each pellet separately by selecting I**ndividual (s)**.

Several transport properties nodes can be added for different fluids in different porous parts for the modeling geometry.

DIFFUSION

Select **Diffusion model** — **Millington and Quirk model** (the default), **Bruggeman model**, **Tortuosity model**, or **User defined** to describe the effective correction of the diffusion coefficient in the pellet. In the case of the **Tortuosity model**, a value for the tortuosity τ_{pe} within the pellet is required. Use this section to specify diffusion models and diffusion coefficients inside the reactive pellet.

From the **Diffusion coefficient** list, select diffusion coefficient for different species. If a **User defined** diffusion model is selected, an **Effective diffusion coefficient** $D_{peff,c}$ (SI unit: m^2/s) is entered. The default value is $1 \cdot 10^{-9}$ m^2/s in both cases.

Diffusion coefficients calculated in Chemistry are available in the list when Chemistry is coupled to the Reactive Pellet Bed feature.

Enter the thermal diffusion coefficients for different species if there is any temperature change within the pellet. The temperature could be coupled to a temperature field solved by a Heat Transfer interface on the same pellet. This can be done by selecting corresponding temperature from **Pellet temperature** list in settings window of Reactive Pellet Bed feature.

Reaction Sources (Reactive Pellet Bed)

The Reaction Sources subnode to the Reactive Pellet Bed is used to define reaction terms to the transport within the reactive pellets. The feature also defines the corresponding averaged heat sources to be applied to heat transport in the bulk fluid.

DOMAIN SELECTION

From the **Selection** list, choose the domains on which to define rate expression or expressions that govern source terms in the transport equations.

Several Reaction Sources nodes can be used to account for different reactions in different parts for the modeling geometry.

REACTION RATES

Select a reaction rate (SI unit: kg/(m^3·s)) for species i from R_{wi} list. Enter a reaction rate expression when User defined is selected from the list. Alternatively, if reaction rate expressions have been defined in a Chemistry interface, they can be chosen from the list.

REACTING VOLUME

When specifying reaction rates for a species in the pellet, the specified reaction rate may have the basis of the pore volume, or the total volume. With the **Pore volume** selected, the reaction expression in kg/(m^3·s) will be multiplied by pellet's porosity ε_{pe}.

HEAT SOURCE

Specify the heat source originating from the heat of reaction of the chemical reactions inside the pellet. When using several pellet types, heat sources for each type can be added.

The heat sources are most conveniently picked up from a Chemistry interface that defines the reaction rate and the heat of reactions. In that case, the heat source expression can be selected from the list. Otherwise you can enter an expression in the text field.

The defined heat source can be used by a Heat Source feature in any of the heat transfer interfaces.

Electrode Surface Coupling

Use this node to define a flux boundary condition based on current densities of one or multiple Electrode Reaction (described in the Electrochmistry Module User's Guide) nodes in an Electrochemistry interface.

The flux is proportional to the current densities and the stoichiometric coefficients according to Faraday's law as defined by summation over the Reaction Coefficients

subnodes. The molar fluxes are multiplied by the species molar masses to obtain the corresponding mass fluxes.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

MASS TRANSFER TO OTHER PHASES

When using the Reacting Flow coupling feature to model coupled momentum and mass transport, boundary conditions that results in a nonnegligible mass flux can be consistently handled by accounting for The Stefan Velocity.

Select **Account for Stefan velocity** to update the Stefan velocity in accordance with the mass flux from the electrode reactions. One example that may benefit from this is when modeling gas diffusion electrodes.

Turbulent Mixing

Use this node to account for the species mixing caused by turbulent flow, typically when the specified velocity field corresponds to a RANS solution. The node defines the turbulent mass diffusion from the turbulent kinematic viscosity and a turbulent Schmidt number.

This node is available if the **Diffusion model** is **Mixture-averaged** or **Fick's law**.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

The **Turbulent Mixing** feature should not be used together with the Reacting Flow coupling feature. In this case the turbulent mixing is added by the coupling feature.

The **Turbulent Mixing** subnode can be added from the context menu (right-click the Transport Properties parent node) or from the **Physics** toolbar, **Attributes** menu.

TURBULENT MIXING

Physics interfaces capable of solving for turbulent fluid flow provide the turbulent kinematic viscosity, and these appear as options in the **Turbulent kinematic viscosity** ν_T

(SI unit: m^2/s) list. The list always contains the **User defined** option that makes it possible to enter any value or expression.

The default **Turbulent Schmidt number** Sc_T is 0.71 (dimensionless).

Reaction

Use the **Reaction** node to specify the reaction kinetics for a single homogeneous chemical reaction. The resulting mass source terms for the species involved in the reaction are automatically defined and added on the selected domains. For turbulent flow, the Reaction node includes the Eddy-dissipation turbulent-reactions model.

REACTION RATE

Select a **Reaction rate** — **Automatic** (the default), or **User defined**. Selecting **Automatic** the laminar flow reaction rate is computed using the mass action law

For **User defined**, input a custom expression or constants for the **Reaction rate** r.

Specify the reaction stoichiometry by entering values for the stoichiometric coefficients (dimensionless) of each species. Enter negative values for reactants and positive values for products.

RATE CONSTANTS

When the **Use Arrhenius expressions** check box is not selected, input custom expressions or constants for the **Forward rate constant** k^{f} and **Reverse rate constant** k^{r}.

When the **Use Arrhenius expressions** check box is selected, enter values for the following parameters of the forward and reverse reactions:

- **Forward frequency factor** A^{f} and **Reverse frequency factor** A^{r} (dimensionless)
- **Forward activation energy** E^{f} and **Reverse activation energy** E^{r}
- **Forward temperature exponent** n^{f} and **Reverse temperature exponent** n^{r} (dimensionless)

TURBULENT FLOW

Note this section is only available when then licensed to the CFD Module (see https://www.comsol.com/products/specifications/).

When the **Turbulent-reaction model** is set to **None**, laminar flow is assumed and the reaction source terms are defined from the reaction stoichiometry and reaction rates prescribed.

When the **Turbulent-reaction model** is set to **Eddy-dissipation**, turbulent flow will be accounted for in the reaction mass sources. In this case, enter values for the **Turbulent reaction model parameters** α_{ED} and β_{ED} (dimensionless).

The **Eddy-dissipation** model also requires an estimation of the turbulent mixing time of the fluid flow turbulence. When a Fluid Flow interface defining it is present in the model, it can be selected from the **Turbulence time scale** list. For example, select **Turbulence time scale (spf/fp1)** to use the time scale defined by the **Fluid Properties** node `fp1` in a Turbulent Flow, k-ε interface with the **Name** set to `spf`.

REGULARIZATION

Select **Rate expression** in order to regularize the individual rate expressions that are added to each species. If the mass fraction for a reactant species ω_i becomes smaller than its **damping limit**, ω_i^{dl}, the rate expression added to species ω_i is reduced linearly. If $\omega_i \leq 0$ for a reactant species, the reaction rate contribution to that species is completely removed. Similarly, the if the mass fraction for a product species ω_j becomes larger than $1 - \omega_j^{\mathrm{dl}}$, the rate expression added to that species is damped linearly. If $\omega_j \geq 1$ for a product species, the reaction rate contribution to that species is completely removed.

The default value for the **damping limit**, ω_i^{dl}, is 10^{-6}, which is appropriate for most applications, but can require adjustment when working with for example catalytic trace species.

Regularization of the rate expressions adds considerable stability to the reaction expressions, but should optimally only be used as a mean to reach convergence. If the regularization is active in too large parts of the domain, the mass balance can become affected since the regularization acts on the contributions to each individual species, not the reaction as a whole.

Reaction Sources

Use the **Reaction Sources** node to define mass source terms from one or more chemical reactions. Both homogeneous reactions as well as heterogeneous reactions occurring in a porous media can be studied. The node also includes the possibility to pick up automatically defined source term definitions from a Chemistry physics interface.

REACTIONS

Add an expression for the reaction mass source, R_i, for each individual species present, except for the one computed from the mass constraint (see Species). Enter a value or expression in the field for the corresponding species.

Select the **Mass transport to other phases** check box if mass is leaving or entering the fluid as a result of the reactions, for instance due to condensation or vaporization in a porous matrix. In this case the mass source for the species calculated from the mass constraint can also be specified. The net mass transfer corresponds to the sum of the mass sources for all species.

REACTING VOLUME

When specifying reaction sources for a species in porous media, the specified mass source may have the basis of the total volume, or the pore volume. For nonporous domains, the **Reacting Volume** setting has no impact.

- For **Total volume**, the reaction mass source expressions are specified per unit volume of the model domain.
- For **Pore volume**, the reaction mass source expressions are specified per unit volume pore space. In this case the reaction mass sources will be multiplied by the domain porosity ε_p (ε_p equals unity for nonporous domains).

Initial Values

The **Initial Values** node adds initial values for the mass fractions that can serve as an initial condition for a transient simulation, or as an initial guess for a nonlinear solver. If required, add additional **Initial Values** nodes from the **Physics** toolbar.

INITIAL VALUES

The initial mass fractions can be specified using a number of quantities. Select the type of input from the **Mixture specification** list. Select:

- **Mass fractions** (the default) to enter mass fractions ($\omega_{0,\omega 1}$ for example)
- **Mole fractions** to enter mole fractions ($x_{0,\omega 1}$ for example)
- **Molar concentrations** (SI unit: $\mathrm{mol/m^3}$) to enter molar concentrations ($c_{0,\omega 1}$ for example)
- **Number densities** (SI unit: $1/\mathrm{m^3}$) to enter number densities ($n_{0,\omega 1}$ for example)
- **Densities** (SI unit: $\mathrm{kg/m^3}$) to enter densities ($\rho_{0,\omega 1}$ for example)

Enter a value or expression in the field for each species except for the one computed from the mass constraint.

INITIAL MIXTURE DENSITY

When the selecting **Molar concentrations**, **Number densities**, or **Densities** are selected from the **Mixture specification** list, the should also be specified. Select **Ideal gas** or **User defined** from the **Initial mixture density** list.

- For **Ideal gas**, also specify the **Initial pressure** p_0 and the **Initial Temperature** T_0. Note that dependent variables solved for are evaluated to zero for initial values. When solving for pressure or temperature together with the mass fractions, apply the initial values from the corresponding interfaces here as well.
- For **User defined**, input a custom for the **Initial mixture density** ρ_{m0}.

Mass Fraction

The **Mass Fraction** node adds boundary conditions for the species mass fractions. For example, the following condition specifies the mass fraction of species *i:* $\omega_i = \omega_{i,0}$.

Set the mass fractions of all species except the one computed from the mass constraint. This ensures that the sum of the mass fractions is equal to one (see Species). This node is available for exterior and interior boundaries.

MASS FRACTION

Specify the mass fraction for each species individually. Select the check box for the species to specify the mass fraction, and enter a value or expression in the corresponding field. To use another boundary condition for a specific species, click to clear the check box for the mass fraction of that species.

MASS TRANSFER TO OTHER PHASES

When using the Reacting Flow coupling feature to model coupled momentum and mass transport, boundary conditions that results in a nonnegligible mass flux can be consistently handled by accounting for The Stefan Velocity.

Select **Account for Stefan velocity** to update the Stefan velocity in accordance with the prescribed mass fractions. Examples of cases that may benefit from this are, for example, when modeling surface reactions or phase change on an exterior boundary.

CONSTRAINT SETTINGS

To display this section, click the **Show** button ( ) and select **Advanced Physics Options**.

Flux

The **Flux** node is available on exterior boundaries and can be used to specify the mass flux. The boundary mass flux for each species is defined in the manner of

$$-\mathbf{n} \cdot \mathbf{j}_i = j_{0,i} \tag{3-127}$$

where $\mathbf{n}$ denotes the outward pointing normal of the boundary. The prescribed flux $j_{0,i}$ can contain an arbitrary flux expression. It can for example be used to represent a *heterogeneous reaction* or a separation process occurring at the boundary. The flux can for example be a function of ω_i, the temperature, the pressure or even the electric potential.

CONVECTION

By default, the flux due to diffusion and migration in an electric field is prescribed. This is the appropriate flux condition when the relative velocity at the boundary is zero. When the fluid velocity is not equal to that of the boundary, for example due to a fluid injection, it is often convenient to prescribe the total flux including convection. To do so select **Include** in the **Convection** section. In this case the prescribed flux is defined as:

$$-\mathbf{n} \cdot (\mathbf{j}_i + \rho \mathbf{u} \omega_i) = J_0$$

MASS TRANSFER TO OTHER PHASES

When using the Reacting Flow coupling feature to model coupled momentum and mass transport, boundary conditions that results in a nonnegligible mass flux can be consistently handled by accounting for The Stefan Velocity.

Select **Account for Stefan velocity** to update the Stefan velocity in accordance with the prescribed flux. Examples of cases that benefit from this are for example when modeling surface reactions or phase change on an exterior boundary. The Stefan velocity represents the mixture velocity resulting from mass fluxes at the wall. This section is not available when **Include** is selected in the **Convection** section.

INWARD FLUX

Specify the **Inward flux** for each species individually. Select the check box for the species to prescribe a flux for and enter a value or expression in the corresponding field. To use another boundary condition for a specific species, click to clear the check box for the flux of that species. Use a positive value for an inward flux.

External convection

Set **Flux type** to **External convection** to prescribe a mass flux to or from an exterior domain (not modeled) assumed to include convection. The exterior can for example include a forced convection to control the temperature or to increase the mass transport. In this case the prescribed mass flux corresponds to

$$j_{0,i} = k_{\omega,i}(\omega_{\mathrm{b},i} - \omega_i) \tag{3-128}$$

where $k_{\omega,i}$ is a mass transfer coefficient and $\omega_{\mathrm{b},i}$ is the bulk mass fraction, the typical mass fraction far into the surrounding exterior domain.

Inflow

The **Inflow** node adds a boundary condition for an inflow boundary, defining the composition of the mixture. The node is available for exterior boundaries. The mixture composition can be specified using the following quantities:

- Mass fractions: $\omega_i = \omega_{0,i}$
- The mole fraction: $x_i = x_{0,i}$
- The molar concentration: $c_i = c_{0,i}$
- The number density, which describes the number of particles per volume: $n_i = n_{0,i}$
- The density: $\rho_i = \rho_{0,i}$
- The mass flow rates.

The node requires input for all species. (The Mass Fraction node can be used to specify boundary mass fractions for a subset of the active species in the interface.)

INFLOW

Select a **Mixture specification**:

- **Mass fractions** (the default) to enter mass fractions ($\omega_{0,\omega 1}$, for example)
- **Mole fractions** to enter mole fractions ($x_{0,\omega 1}$ for example)
- **Molar concentrations** (SI unit: $\mathrm{mol/m^3}$) to enter molar concentrations ($c_{0,\omega 1}$, for example)
- **Number densities** (SI unit: $1/\mathrm{m^3}$) to enter number densities ($n_{0,\omega 1}$, for example)
- **Densities** (SI unit: $\mathrm{kg/m^3}$) to enter densities ($\rho_{0,\omega 1}$, for example)
- **Mass flow rates** (SI unit: kg/s) to enter the total mass flow over the boundary ($J_{in,\omega 1}$, for example)

Enter a value or expression in the field for each species except for the one computed from the mass constraint.

CONSTRAINT SETTINGS

To display this section, click the **Show** button ( ) and select **Advanced Physics Options**.

No Flux

The **No Flux** node is the default boundary condition available for exterior boundaries. It should be used on boundaries across which there is no mass flux, typically exterior solid walls where no surface reactions occur. The condition applied for each species corresponds to

$$-\mathbf{n} \cdot \mathbf{j}_i = 0$$

where $\mathbf{n}$ denotes the outward pointing normal of the boundary.

Outflow

The **Outflow** node is the preferred boundary condition at outlets where the species are to be transported out of the model domain. It is useful, for example, in mass transport models where it is assumed that convection is the dominating effect driving the mass flow through the outflow boundary. This node is available for exterior boundaries. The boundary condition is applied to all species and corresponds to one of the following equations depending on the selected diffusion model:

- For the Maxwell–Stefan Diffusion Model:

$$-\mathbf{n} \cdot \rho \omega_i \sum_k D_{ik} \mathbf{d}_k = 0$$

- For the Mixture-Averaged Diffusion Model:

$$-\mathbf{n} \cdot \rho D_i^m \nabla \omega_i = 0$$

- For the Fick's Law Diffusion Model:

$$-\mathbf{n} \cdot \rho D_i^f \nabla \omega_i = 0$$

Symmetry

The **Symmetry** node can be used to represent boundaries where the species concentration is symmetric; that is, there is no mass flux in the normal direction across the boundary:

$$-\mathbf{n} \cdot \mathbf{N} = -\mathbf{n} \cdot (\rho \omega_i \mathbf{u} + \mathbf{j}_i) = 0$$

This boundary condition is identical to the No Flux node, but applies to all species and cannot be applied to individual species. The Symmetry node is available for exterior boundaries.

Flux Discontinuity

The **Flux Discontinuity** node represents a discontinuity in the mass flux across an interior boundary:

$$-\mathbf{n} \cdot (\mathbf{N}_\mathrm{d} - \mathbf{N}_\mathrm{u}) = N_0 \qquad \mathbf{N} = (\rho \omega_i \mathbf{u} + \mathbf{j}_i)$$

where the value of N_0 specifies the size of the flux jump evaluated from the down to the upside of the boundary.

FLUX DISCONTINUITY

Specify the jump in species mass flux. Use a positive value for increasing flux when going from the downside to the upside of the boundary. The boundary normal points in the direction from the downside to the upside of an interior boundary and can be plotted for visualization.

Select the **Species** check boxes to specify a flux discontinuity, and enter a value or expression for the **Flux discontinuity** N_0 (SI unit: kg/(m^2·s)) in the corresponding field, $N_{0,\,\mathrm{w1}}$ for example. To use a different boundary condition for a specific species, click to clear the check box for the flux discontinuity of that species.

Open Boundary

Use the **Open Boundary** node to set up mass transport across boundaries where both convective inflow and outflow can occur. Use the node to specify an exterior species composition on parts of the boundary where fluid flows into the domain. A condition equivalent to the Outflow node applies to the parts of the boundary where fluid flows out of the domain. The direction of the flow across the boundary is typically calculated by a Fluid Flow interface and is entered as Model Inputs.

EXTERIOR COMPOSITION

Enter a value or expression for the species composition. Select:

- **Mass fractions** (the default) to enter mass fractions ($\omega_{0,\omega 1}$, for example)
- **Mole fractions** to enter mole fractions ($x_{0,\omega 1}$, for example)
- **Molar concentrations** (SI unit: $\mathrm{mol/m^3}$) to enter molar concentrations ($c_{0,\omega 1}$, for example)
- **Number densities** (SI unit: $1/\mathrm{m^3}$) to enter number densities ($n_{0,\omega 1}$, for example) and to describe the number of particles per volume $n = n_0$
- **Densities** (SI unit: $\mathrm{kg/m^3}$) to enter densities ($\rho_{0,\omega 1}$, for example)

A concentration quantity other than the mass fractions can only be used when all species are defined.

Equilibrium Reaction

Use this node to model a reaction where the kinetics is assumed so fast that the equilibrium condition is fulfilled at all times. The node solves for an additional degree of freedom (the reaction rate R_{eq}) to fulfill the equilibrium condition at all times in all space coordinates.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

EQUILIBRIUM CONDITION

Selecting **Equilibrium constant** in the list, the following equilibrium condition based on the species activities and the law of mass action is used

$$K_{\mathrm{eq}} = \frac{\prod_{i \in \text{ products}} a_i^{\nu_i}}{\prod_{i \in \text{ reactants}} a_i^{-\nu_i}}$$

where ν_i are the stoichiometric coefficients and the species activities are defined from the concentration, c_i, and the unit activity concentration c_{a0}.

$$a_i = \frac{c_i}{c_{a0}}$$

Enter a value or expression for the dimensionless **Equilibrium constant** K_{eq}, and the **Unit activity concentration** C_{a0}.

Select **User defined** from the list to instead enter a manually defined **Equilibrium expression** E_{eq}.

STOICHIOMETRIC COEFFICIENTS

Enter a value for the stoichiometric coefficient ν for all participating species. Use negative values for reactants and positive values for products in the modeled reaction. Species with a stoichiometric coefficient value of 0 are not affected by the **Equilibrium Reaction** node.

Surface Equilibrium Reaction

Use this node to model an equilibrium reaction on a boundary (surface). The kinetics of the reaction is assumed so fast that the equilibrium condition is fulfilled at all times. The node solves for an additional degree of freedom (the mass flux J_{eq}) to fulfill the equilibrium condition at all times in all space coordinates along the boundary.

This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

The settings for this node are the same as for Equilibrium Reaction except for the setting in the section below.

MASS TRANSFER TO OTHER PHASES

When using the Reacting Flow coupling feature to model coupled momentum and mass transport, boundary conditions that results in a nonnegligible mass flux can be consistently handled by accounting for The Stefan Velocity. Select **Account for Stefan velocity** to update the Stefan velocity in accordance with the prescribed mass fractions. Examples of cases that may benefit from this are for example when modeling surface reactions or phase change on an exterior boundary.

The Nernst–Planck Equations Interface

Ionic solutions subjected to electric fields are affected by migration transport in addition to the existing mass transport by diffusion and convection. Migration implies that positive ions migrate from positive to negative potential, and vice versa for negatively charged ions. The flux of the ionic species i in the solution is given by the mass flux vector (SI unit: mol/(m^2·s))

$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_{\mathrm{m},i} F c_i \nabla V + c_i \mathbf{u} \tag{3-129}$$

where c_i denotes the concentration of species i (SI unit: mol/ m^3), D_i is the diffusion coefficient of species i (SI unit: m^2/s), $\mathbf{u}$ is the solvent velocity (SI unit: m/s), F refers to Faraday's constant (SI unit: s·A/mol), V denotes the electric potential (SI unit: V), z_i is the charge number of the ionic species (dimensionless), and $u_{\mathrm{m},i}$ its ionic mobility (SI unit: s·mol/kg).

There are three physics interfaces for this type of transport. In the **Nernst–Planck Equations (npe)** interface ( ), found under the **Chemical Species Transport** branch ( ) when adding a physics interface, the transport of every charged species is accounted for, and is solved for in combination with the electroneutrality condition.

The Nernst–Planck Equations interface supports modeling of transport by convection, diffusion, and migration of dissolved ionic species in 1D, 2D, and 3D as well as for axisymmetric models in 1D and 2D. The dependent variables are the species concentrations, c_i, and the electric potential, V. The physics interface is tailored for modeling of electrochemical cells and corrosion processes and offers a straightforward way to perform tertiary current distribution analysis.

The physics interface has the equations, boundary conditions, and rate expression terms for modeling mass transport of ionic species by convection, diffusion, and migration, solving for the species concentrations and the electric potential. The main feature is the Convection, Diffusion, and Migration node, which adds the equation for the species concentration and the potential and provides an interface for defining species properties and model inputs.

When this physics interface is added, these default physics nodes are also added to the **Model Builder** — **Convection, Diffusion and Migration**, **No Flux** (the default boundary condition for species concentrations), **Electric Insulation** (the default boundary

condition for the electric field), and **Initial Values**. Then, from the **Physics** toolbar, add other nodes that implement, for example, boundary conditions and rate expression terms. You can also right-click **Nernst–Planck Equations** to select physics features from the context menu.

SETTINGS

The **Label** is the default physics interface name.

The **Name** is used primarily as a scope prefix for variables defined by the physics interface. Refer to such physics interface variables in expressions using the pattern `<name>.<variable_name>`. In order to distinguish between variables belonging to different physics interfaces, the `name` string must be unique. Only letters, numbers, and underscores (_) are permitted in the **Name** field. The first character must be a letter.

The default **Name** (for the first physics interface in the model) is `npe`.

SPECIES

Select the species that the physics interface computes from the electroneutrality condition in Equation 3-129. That is, its value comes from the fact that the net charge in every control volume is zero. Select the preferred species in the **From electroneutrality** list. To minimize the impact of any numerical errors, use the species with the highest concentration. By default, the software uses the first species.

DEPENDENT VARIABLES

Add or remove species in the model and also change the names of the dependent variables that represent the species concentrations.

Specify the **Number of species**. There must be at least two species. To add a single species, click the **Add species** button ( ). To remove a species, select it in the list and click the **Remove species** button ( ).Edit the names of the species directly in the table.

The species are dependent variables, and their names must be unique with respect to all other dependent variables in the model.

ADVANCED SETTINGS

To display this section, click the **Show More Options** button ( ) and select **Advanced Physics Options**. Normally these settings do not need to be changed. Select a **Convective term** — **Nonconservative form** (the default) or **Conservative form**.

Convective Term Formulation

DISCRETIZATION

To display all settings available in this section, click the **Show More Options** button ( ) and select **Advanced Physics Options**.

For more information about these settings, see the *Discretization* section under The Transport of Diluted Species Interface.

CONSISTENT AND INCONSISTENT STABILIZATION

To display this section, click the **Show More Options** button ( ) and select **Stabilization**. Any settings unique to this physics interface are listed below.

The crosswind diffusion implementation used in the Nernst–Planck Equations interface is based on Codina (Ref. 1).

- When the **Crosswind diffusion** check box is selected, the **Lower gradient limit** g_{lim} (SI unit: mol/m^4) field defaults to `0.1[mol/m^3)/npe.helem`, where `npe.helem` is the local element size.
- For both consistent stabilization methods, select an **Equation residual**. **Approximate residual** is the default setting and it means that derivatives of the diffusion tensor components are neglected. This setting is usually accurate enough and is faster to compute. If required, select **Full residual** instead.

- Domain and Boundary Nodes for the Nernst–Planck Equations Interface
- Theory for the Nernst–Planck Equations Interface
- Convective Term Formulation

In the *COMSOL Multiphysics Reference Manual* see Table 2-4 for links to common sections and Table 2-5 to common feature nodes. You can also search for information: press F1 to open the **Help** window or Ctrl+F1 to open the **Documentation** window.

Domain and Boundary Nodes for the Nernst–Planck Equations Interface

The Nernst–Planck Equations Interface has these domain and boundary physics nodes available.

DOMAIN NODES

- Convection, Diffusion, and Migration
- Reactions
- Equilibrium Reaction is described for the Transport of Diluted Species interface
- Initial Values

BOUNDARY CONDITIONS

In the Nernst–Planck Equations interface, there are separate boundary conditions for the species concentrations and for the electric potential. This means that there are two active boundary conditions on each boundary. Many different combinations of boundary conditions can be set for the electric field and concentration fields on a boundary, but not all combinations are relevant.

SPECIES CONCENTRATION BOUNDARY CONDITIONS

The following boundary conditions for the species concentrations are available on exterior boundaries:

- Concentration
- Flux
- No Flux (the default boundary condition for species concentrations)
- Symmetry
- Inflow
- Outflow

For interior boundaries, continuity in the concentration of all species is the default boundary condition. In addition, the Flux Discontinuity boundary condition is available on interior boundaries.

ELECTRIC POTENTIAL BOUNDARY CONDITIONS

The following boundary conditions for the electric potential are available on exterior boundaries:

- Current Density
- Electric Insulation (the default boundary condition for the electric potential)
- Electric Potential (described for the Electrostatics interface in the *COMSOL Multiphysics Reference Manual*)

For interior boundaries, continuity in the electric potential is the default boundary condition. In addition, the following boundary conditions are available on interior boundaries:

- Current Discontinuity
- Electric Potential (described for the Electrostatics interface in the *COMSOL Multiphysics Reference Manual*)

EDGES AND POINTS

The Point Mass Source and Line Mass Source features are also available and described for the Transport of Diluted Species interface.

The links to the physics nodes described in the *COMSOL Multiphysics Reference Manual* do not work in the PDF, only from the online help.

For axisymmetric models, COMSOL Multiphysics takes the axial symmetry boundaries (at $r = 0$) into account and automatically adds an **Axial Symmetry** node to the model that is valid on the axial symmetry boundaries only.

Convection, Diffusion, and Migration

The **Convection, Diffusion, and Migration** is the main physics interface node which adds the concentration and electric field variables and the Nernst–Planck equations governing them.

MODEL INPUTS

The temperature model input is always available, and set to **Common model input** by default. Select the source of the **Temperature** field T:

- Select **User defined** to enter a value or an expression for the temperature (SI unit: K). This input is always available.
- If required, select a temperature defined by a Heat Transfer interface present in the component (if any). For example, select **Temperature (ht)** to use the temperature defined by the Heat Transfer in Fluids interface with the `ht` name.

CONVECTION

This section is available when the **Convection** check box is selected.

The velocity field for the convection of the solvent, which is used in the convective term, needs to be specified as feature input. Select the source of the **Velocity field** $\mathbf{u}$:

- Select **User defined** to enter values or expressions for the velocity components. This input is always available.
- Select a velocity field defined by a Fluid Flow interface present in the model (if any). For example, select **Velocity field (spf)** to use the velocity field defined by the **Fluid Properties** node `fp1` in a Single-Phase Flow, Laminar Flow interface with `spf` as the Name.

DIFFUSION

Select a **Material** from the list (when applicable and available). The default is **None**.

Specify the **Diffusion coefficient** D_i for each species. This can be a scalar value for isotropic diffusion or a tensor describing anisotropic diffusion. Enter the values in the field (one for each species).

MIGRATION IN ELECTRIC FIELD

Specify the **Mobility** and the **Charge number** of the ionic species. These properties affect the migration of ionic species. By default the **Mobility** is set to be calculated based on the species diffusivities and the temperature using the **Nernst–Einstein relation**. To manually specify the mobility, select **User defined** for the mobility $u_{m,i}$ and enter one value for each species.

Enter the **Charge number** z_i (dimensionless, but requires a plus or minus sign) for each species.

Specify the temperature (if you are using mobilities based on the Nernst–Einstein relation) in the **Model Inputs** section.

Electric Insulation

The **Electric Insulation** node is the default boundary condition for the electric field. It provides a boundary condition for the electric field that means that the boundary is electrically insulated; that is, there is no current flowing across the boundary:

$$-\mathbf{n} \cdot \mathbf{i} = 0 \tag{3-130}$$

No Flux

The **No Flux** node is the default boundary condition on exterior boundaries. It should be used on boundaries across which there is no mass flux, typically exterior solid walls where no surface reactions occur. The condition applied for each species corresponds to

$$-\mathbf{n} \cdot (-D\nabla c - zu_{\mathrm{m}}Fc\nabla V) = 0$$

where $\mathbf{n}$ denotes the outward pointing normal of the boundary.

CONVECTION

By default, the feature prescribes a vanishing flux due to diffusion and migration in an electric field. This is the appropriate no flux condition when the relative convective velocity at the boundary is zero. When the fluid velocity at the boundary is not equal to that of the boundary, it is often convenient to prescribe the total flux including the convection. To do this select **Include** in the **Convection** section. In this case the no flux condition is:

$$-\mathbf{n} \cdot (-D\nabla c - zu_{\mathrm{m}}Fc\nabla V + \mathbf{u}c) = 0$$

Initial Values

The **Initial Values** node adds initial values for the concentrations c_i and the electric potential V that can serve as an initial condition for a transient simulation or as an initial guess for a nonlinear solver. Add more **Initial Values** nodes from the **Physics** toolbar.

INITIAL VALUES

Enter values or expressions for the initial value of the **Concentration** c_i (SI unit: mol/m^3) (except the one that a mass constraint determines) and for the **Electric potential** V (SI unit: V). The default concentration values are 0 mol/m^3 and the default electric potential is 0 V.

Reactions

In order to account for consumption or production of species, the **Reactions** node adds rate expressions R_i, which appear on the right-hand side of the species transport equations.

REACTIONS

Add a rate expression R_i (SI unit: mol/(m^3·s)) for each of the species solved for. Enter a value or expression in the field of the corresponding species.

Concentration

The **Concentration** node adds a boundary condition for the species concentrations: for example the following condition specifies the concentration of species, c_i:

$$c_i = c_{i,0}$$

Set the concentration of all species except the one computed from the electroneutrality condition, which ensures that the net charge is zero. See Species.

CONCENTRATION

Specify the concentration c_i (SI unit: mol/m^3) for each species individually. Select the check box for the species to specify the concentration, and enter a value or expression in the corresponding field. To use another boundary condition for a specific species, click to clear the check box for that species' mass fraction.

CONSTRAINT SETTINGS

To display this section, click the **Show More Options** button ( ) and select **Advanced Physics Options**.

Flux

The **Flux** node can be used to specify the species flux across a boundary. The species flux, for example at the surface of a electrode, is defined as:

$$-\mathbf{n} \cdot (-D\nabla c - zu_{\mathrm{m}}Fc\nabla V) = J_0$$

where $\mathbf{n}$ denotes the outward pointing normal of the boundary. The flux J_0 can be any function of concentration and electric potential (and indeed temperature if heat transfer is included in the model), often provided by a kinetic expression. In electrochemistry, this function usually depends on concentration and exponentially on the electric potential through either the Tafel equation or the *Butler-Volmer equation*.

CONVECTION

By default, the flux due to diffusion and migration in an electric field is prescribed. This is the appropriate flux condition when the relative velocity at the boundary is zero. When the fluid velocity is not equal to that of the boundary, it is often convenient to prescribe the total flux, including the convection. To do this select **Include** in the **Convection** section. When including the convection, the prescribed flux is defined as:

$$-\mathbf{n} \cdot (-D\nabla c - zu_{\mathrm{m}}Fc\nabla V + \mathbf{u}c) = J_0$$

INWARD FLUX

Specify the inward species flux for each species individually. Select the check box for the species to prescribe a flux for and enter a value or expression for the **Inward flux** J_0. To use another boundary condition for a specific species, click to clear the check box for that species' flux. Use a positive value for an inward flux.

Symmetry

The **Symmetry** node can be used to represents a boundaries where the concentration is symmetric; that is, there is no species flux in the normal direction across the boundary. This boundary condition is identical to that of the No Flux condition.

Inflow

The **Inflow** node adds a boundary condition for an inflow boundary, where the concentration for all species is specified in the manner of $c_i = c_{i,0}$.

This condition is identical to the Concentration node, but is applied to all species and cannot be applied to individual species.

CONCENTRATION

Specify the concentration c_i (SI unit: $\mathrm{mol/m^3}$) of each species individually by entering a value or expression in the corresponding field.

BOUNDARY CONDITION TYPE

The option **Concentration constraint** constrains the concentration values on the boundary by the use of pointwise constraints.

The other option, **Flux (Danckwerts)** can be used when the concentration at the boundary is not known, or when it varies in a non-trivial manner. This may, for example, be useful when reactions with high reaction rates occur in the vicinity of the inlet. In this case the concentration far upstream of the boundary is instead prescribed. The **Flux (Danckwerts)** condition prescribes the total flux defined by the upstream concentration and the fluid velocity at the boundary.

Danckwerts Inflow Boundary Condition

CONSTRAINT SETTINGS

To display this section, click the **Show More Options** button ( ) and select **Advanced Physics Options** in the **Show More Options** dialog box.

Outflow

The **Outflow** condition assumes that convection and migration is the dominating transport mechanism across the outflow boundary, and therefore that diffusive transport can be ignored, that is:

$$\mathbf{n} \cdot (-D\nabla c) = 0$$

Flux Discontinuity

The **Flux Discontinuity** node represents a discontinuity in the species flux across an interior boundary:

$$-\mathbf{n} \cdot (\mathbf{N}_u - \mathbf{N}_d) = N_{0,i} \qquad \mathbf{N} = (c_i \mathbf{u} + \mathbf{J}_i)$$

where the value of $N_{0,}i$ specifies the size of the flux jump, evaluated from the up to the down side of the boundary. This boundary condition is only available on interior boundaries.

FLUX DISCONTINUITY

Specify the jump in species flux, using a positive value for increasing flux when going from the down to the up side of the boundary. The normal direction `(nx,ny,nz)` (`(nr,nz)` in axisymmetric models) points in the direction from the downside toward the upside of an interior boundary and can be plotted for visualization.

Select the check boxes for the species to specify a **Flux discontinuity** N_0 (SI unit: mol/(m^2·s)) and enter a value or expression for the mass flux jump in the corresponding field. To use another boundary condition for a specific species, click to clear the check box for that species' flux discontinuity.

Current Density

The **Current Density** node provides a boundary condition for the electric field which makes it possible to set the total current density at a boundary. The condition is defined as:

$$-\mathbf{n} \cdot \mathbf{i} = i_0 \tag{3-131}$$

where $\mathbf{n}$ denotes the normal vector to the boundary and i_0 is the inward current density.

It is common to combine this boundary condition with concentration conditions for the species. Such a combination is useful in cases where the flow in an electrochemical cell is vigorous and in cases where the whole cell is not treated in a model, most often when the opposite electrode is a far away. Half-cell investigations are very applicable for this type of condition.

INWARD CURRENT DENSITY

Specify the current density i_0 (SI unit: A/m^2). Use a positive value for an inward current flow.

Current Discontinuity

The **Current Discontinuity** node represents a discontinuity in the current density across an interior boundary:

$$-\mathbf{n}\cdot(\mathbf{i}_u-\mathbf{i}_d)=i_0 \qquad \mathbf{i}=F\sum_{k=1}^{n} z_i(-D_i\nabla c_i - z_i u_{m,i} F c_i \nabla V)$$

where the value of $\mathbf{i}_0$ specifies the size of the current density jump evaluated from the up to the down side of the boundary. This boundary condition is only available on interior boundaries.

CURRENT DISCONTINUITY

Specify i_0 (SI unit: A/m^2), the jump in current density, using a positive value for increasing current density when going from the up to the down side of the boundary. The normal direction `(nx,ny,nz)` (`(nr,nz)` in axisymmetric models) points in the direction from the downside toward the upside of an interior boundary and can be plotted for visualization.

Open Boundary

Use the **Open Boundary** node to set up mass transport across boundaries where both convective inflow and outflow can occur. Specify an exterior species concentration on parts of the boundary where fluid flows into the domain. A condition equivalent to the Outflow node applies to parts of the boundary where fluid flows out of the domain.

The direction of the flow across the boundary is typically calculated by a Fluid Flow interface, and is provided as a Model Input to the Nernst–Planck Equations interface.

The potential is assumed to be constant in the normal direction across the boundary.

EXTERIOR CONCENTRATION

Enter a value or expression for the exterior concentration $c_{0,c2}$ (SI unit: mol/m^3).

Reference for the Nernst–Planck Equations Interface

1. R. Codina, "A Discontinuity-capturing Crosswind-dissipation Stabilization for the Finite Element Solution of the Convection-diffusion Equation", *Computer Methods in Applied Mechanics and Engineering*, vol. 110, pp. 325–342, 1993.

The Nernst–Planck-Poisson Equations Interface

The **Nernst-Planck-Poisson Equations** interface ( ), found under the **Chemical Species Transport** branch ( ) when adding a physics interface, is a predefined multiphysics interface for modeling transport of electrolyte species without the otherwise common assumption of local electroneutrality. This allows for simulating charge separation that typically arises close to an electrode surface, where ions in the electrolyte are attracted and repelled by unscreened excess charge on the electrode. The charge separation region, also called the diffuse double layer, normally extends a few nanometers away from the electrode surface into the electrolyte. The study of the charge separation is important to applications that consider very thin layers of electrolyte, such as electrochemical capacitors, atmospheric corrosion problems, ion-selective field effect transistors (ISFETs), and nanoelectrochemistry.

The Nernst–Planck–Poisson Equations predefined multiphysics interface adds ( ) (with Migration enabled), which solves for the Nernst–Planck equations without charge neutrality, and The Electrostatics Interface( ), that solves for the Poisson's equation.

A ( ) multiphysics node is also added. This node computes the local space charge, based on the local concentrations and species charges in the Transport of Diluted Species interface, and adds it to Poisson's Equation in the Electrostatics interface.

Finally, a ( ) multiphysics node is added that applies the potential dependent variable in the Electrostatics interface into the migration term of the Transport of Diluted Species interface.

	• The Multiphysics Branch in the *COMSOL Multiphysics Reference Manual.* • The Transport of Diluted Species Interface • The Electrostatics Interface
	Diffuse Double Layer: Application Library path **Chemical_Reaction_Engineering_Module/Electrokinetic_Effects/diffuse_double_layer**

The Electrophoretic Transport Interface

The **Electrophoretic Transport (el)** interface ( ), found under the **Chemical Species Transport** branch ( ), is used to solve for the electrophoretic transport of an arbitrarily number of species in water-based system, subject to potential gradients. The species transported can be any combination of weak and strong acids and bases, ampholytes, and uncharged species. The transport of masses and charge is based on the Nernst–Planck equations for molecular transport, in combination with electroneutrality, dissociation equilibria for weak acids, bases and ampholytes as well as the water auto-ionization reaction.

The physics interface can simulate most forms of electrophoresis modes, such as zone electrophoresis, isotachophoresis, isoelectric focusing, and moving boundary electrophoresis.

Gel electrophoresis can be simulated by the inclusion of immobile charged species.

The interface supports simulation in 1D, 2D, and 3D as well as for axisymmetric components in 1D and 2D.

The dependent variables are the electrolyte potential, and the molar concentrations of the included species, added individual by each species node in the model tree.

Zone Electrophoresis: Application Library path **Chemical_Reaction_Engineering_Module/Electrokinetic_Effects/zone_electrophoresis**

SETTINGS

The **Label** is the default physics interface name.

The **Name** is used primarily as a scope prefix for variables defined by the physics interface. Refer to such physics interface variables in expressions using the pattern `<name>.<variable_name>`. In order to distinguish between variables belonging to different physics interfaces, the `name` string must be unique. Only letters, numbers, and underscores (_) are permitted in the **Name** field. The first character must be a letter.

The default **Name** (for the first physics interface in the model) is `el`.

DOMAIN SELECTION

If any part of the model geometry should not partake in the mass transfer model, remove that part from the selection list.

OUT-OF-PLANE THICKNESS

For 2D components, enter a value or expression for the out-of-plane **Thickness** d (SI unit: m). The value of d determines the size of the domain perpendicular to the modeled 2D cross section. This value yields, for example, the correct total current when the current density is obtained from a 2D simulation.

CROSS SECTIONAL AREA

For 1D components, enter a **Cross sectional area** A_c (SI unit: m^2) to define a parameter for the area of the geometry perpendicular to the 1D component. The value of this parameter is used, among other things, to automatically calculate the total current from the current density vector. The analogy is valid for other fluxes. The default is 1 m^2.

TRANSPORT MECHANISMS

Mass transport due to diffusion and migration is always included. Use the check boxes available under **Additional transport mechanisms** to control other transport mechanisms.

- By default, the **Convection** check box is selected. Clear the check box to disable convective transport.
- The **Mass transfer in porous media** check box activates functionality specific to species transport in porous media. When selected, the Porous Matrix Properties node can be added to a domain to specify the electrolyte volume fraction and tortuosity, and the Effective Transport Parameter Correction sections are enabled in the species nodes.

CONSISTENT STABILIZATION

To display this sections, click the **Show More Options** button ( ) and select **Stabilization** in the **Show More Options** dialog box.

- When the **Crosswind diffusion** check box is selected, a weak term that reduces spurious oscillations is added to the transport equation. The resulting equation system is always nonlinear.
- For both **Streamline diffusion** and **Crosswind diffusion**, select an **Equation residual**. **Approximate residual** is the default and means that derivatives of the diffusivity are neglected. This setting is usually accurate enough and is computationally faster. If required, select **Full residual** instead.

INCONSISTENT STABILIZATION

To display this section, click the **Show More Options** button ( ) and select **Stabilization** in the **Show More Options** dialog box. By default, the **Isotropic diffusion** check box is not selected, because this type of stabilization adds artificial diffusion and affects the accuracy of the original problem. However, this option can be used to get a good initial guess for under-resolved problems.

ADVANCED SETTINGS

To display this section, click the **Show More Options** button ( ) and select **Advanced Physics Options** in the **Show More Options** dialog box. Normally these settings do not need to be changed. Select a **Convective term** — **Nonconservative form** (the default) or **Conservative form**. The conservative formulation should be used for compressible flow.

DISCRETIZATION

To display all settings available in this section, click the **Show More Options** button ( ) and select **Advanced Physics Options** in the **Show More Options** dialog box.

The concentration variables are set to use Linear elements by default.

The potential variable is set to use Quadratic elements by default.

The **Compute boundary fluxes** check box is activated by default so that COMSOL Multiphysics computes predefined accurate boundary flux variables. When this option is checked, the solver computes variables storing accurate boundary fluxes from each boundary into the adjacent domain.

If the check box is cleared, the COMSOL Multiphysics software instead computes the flux variables from the dependent variables using extrapolation, which is less accurate

in postprocessing results but does not create extra dependent variables on the boundaries for the fluxes.

The flux variables affected in the interface are:

- `<name>.nIl`, where `<name>` is the name of the interface (default is `el`), set on the interface top node. This is the normal electrolyte current density.
- `<name>.ntflux_<species_name>` is the **Species name** (see Common Settings for the Species Nodes in the Electrophoretic Transport Interface below). This is the normal total flux for each species.

Also the **Apply smoothing to boundary fluxes** check box is available if the previous check box is checked. The smoothing can provide a more well-behaved flux value close to singularities.

For details about the boundary fluxes settings, see Computing Accurate Fluxes in the *COMSOL Multiphysics Reference Manual*.

Regarding the **Value type when using splitting of complex variables**, see Splitting Complex-Valued Variables in the *COMSOL Multiphysics Reference Manual*.

DEPENDENT VARIABLES

The dependent variable name for the electrolyte potential variable is `phil` by default.

The name of the concentration dependent variables are named as `el.xxx`, where the `el` is the name of the interface as set above, and the `xxx` string is controlled by the **Species name** setting on the individual species nodes.

FURTHER READING

- Theory for the Electrophoretic Transport Interface
- Numerical Stabilization in the *COMSOL Multiphysics Reference Manual*.
- In the *COMSOL Multiphysics Reference Manual*, see Table 2-4 for links to common sections and Table 2-5 for common feature nodes. You can also search for information: press F1 to open the **Help** window or Ctrl+F1 to open the **Documentation** window.

Common Settings for the Species Nodes in the Electrophoretic Transport Interface

The interface features the following species nodes, applicable on the domain level:

- Ampholyte
- Fully Dissociated Species
- Uncharged Species
- Weak Acid
- Weak Base

Each species node add a dependent variable for the concentration. The initial and boundary condition, as well as adding additional source reaction terms, for each species concentration is controlled by adding subnodes to the species nodes:

- Concentration
- Flux
- Inflow
- Initial Concentration
- No Flux
- Outflow
- Species Source

The Ampholyte, Weak Acid, and Weak Base nodes are dissociation species and may define an arbitrary number of dissociation steps. Each dissociation step is defined by its $\mathrm{p}K_a$ (the acid equilibrium constant) parameter. For the weak bases the $\mathrm{p}K_a$ refers to the acid constant of the conjugate acid. Each dissociation step adds one additional subspecies concentration variable so that the concentration dependent variable represents the sum of all subspecies, and initial and boundary conditions are defined with respect to this total concentration.

All species node have a setting for the **Species name**, which needs to be unique. The species name is used for naming of all related variables of the species. For species nodes not defining any subspecies, the concentration variables are named as `<name>.c_<species_name>` where `<name>` is the name of the interface (default is `el`), set on the interface top node, and `<species_name>` is the **Species name**. For dissociation species nodes defining multiple subspecies, the concentration nodes are named as `<name>.c<X>_<species_name>` where `<X>` is the integer from 1 up to the

total number of subspecies. Note that the Solvent node automatically defines the concentration variables for protons (`<name>.cH`) and hydroxide ions (`<name>.cOH`).

All species except the Uncharged Species carry charge and contribute to the total electrolyte current which is used in the equation for solving the electrolyte potential.

The **Immobile Species** check box can be used to lock the concentration of a species, to, for instance, define the immobile charges in a ion-selective membrane or a gel. When the check box is enabled the concentration of the species is not added as a dependent variable to the model; instead the concentration will be set to the value provided in the **Concentration** field. The contribution to the electrolyte current for immobile species is zero.

Diffusion and Migration Settings

All species, except when the **Immobile Species** check box has been enabled, may be transported by diffusion, and charged species are also transported by migration in the electric field.

For dissociation species you may choose to set the transport parameters to be the **Same for all species** appearing in the different dissociation steps, or you may use **Individual** settings for each subspecies.

Typically the mobilities and diffusivities for small species are related by the **Nernst-Einstein relation**, and when this relation is enabled you can choose whether to specify either the **Diffusivity** (SI unit: m^2/s) or the **Mobility** (SI-unit: s·mol/kg). The **Debye-Hückel-Henry** relation is commonly used for larger molecules, such as proteins.

Note: There are other definitions of the migration transport equations in literature which use mobilities expressed in $m^2/(V \cdot s)$, whereas COMSOL Multiphysics uses s·mol/kg. To convert mobilities expressed in $m^2/(V \cdot s)$ to the corresponding values in s·mol/kg, you typically divide by the Faraday constant, `F_const` (about 96,485 C/mol).

EFFECTIVE TRANSPORT PARAMETER CORRECTION

If **Mass transfer in porous media** is enabled on the interface top node, you may use the settings of this section in the species nodes to account for the changed mass transport in a porous domain due to the lowered porosity and the increased tortuosity.

The default correction model is **Bruggeman**, which multiplies the diffusivity and mobility values by the porosity to the power of 1.5. The porosity of a domain is set by the Porous Matrix Properties node.

IONIC STRENGTH CONTRIBUTION

To display this section, click the **Show More Options** button ( ) and select **Advanced Physics Options** in the **Show More Options** dialog box.

The **Debye-Hückel-Henry** relation makes use of the ionic strength for calculating the species mobility from the diffusivity. All charged species contribute to the ionic strength, either assuming the species contributing to an **Ideal solution** or by using the **Lindestrøm-Lang** assumption. The latter is usually used for macromolecules.

Domain, Boundary, and Pair Nodes for the Electrophoretic Transport Interface

The interface has the following domain, boundary, and pair nodes, listed in alphabetical order, available from the **Physics** ribbon toolbar (Windows users), **Physics** context menu (Mac or Linux users), or by right-clicking to access the context menu (all users).

To add a node, go to the **Physics** toolbar, no matter what operating system you are using. Subnodes are available by clicking the parent node and selecting it from the **Attributes** menu.

- Ampholyte
- Concentration
- Current
- Current Density
- Current Source
- Flux
- Fully Dissociated Species
- Inflow
- Initial Concentration
- Initial Potential
- Insulation
- No Flux
- Outflow
- Porous Matrix Properties
- Potential
- Protein
- Species Source
- Solvent
- Uncharged Species
- Weak Acid
- Weak Base

For axisymmetric components, COMSOL Multiphysics takes the axial symmetry boundaries (at $r = 0$) into account and automatically adds an **Axial Symmetry** node that is valid on boundaries representing the symmetry axis.

In the *COMSOL Multiphysics Reference Manual*, see Table 2-4 for links to common sections and Table 2-5 for common feature nodes. You can also search for information: press F1 to open the **Help** window or Ctrl+F1 to open the **Documentation** window.

Solvent

The settings of this node are used to define the properties of the aqueous solvent.

If Convection is enabled on the interface top node, you can specify the **Velocity field** (m/s) as user defined input using analytical expressions or the velocity field variables solved for by a separate physics interface.

The Solvent node automatically defines the concentration variables and for protons (`<name>.cH`) and hydroxide ions (`<name>.cOH`), and the corresponding flux expressions. See Diffusion and Migration Settings for how to set up the transport parameters for the proton and hydroxide ions.

In the **Solvent Properties** section you can modify the **Dynamic viscosity** (Pa·s) and **Relative permittivity** (unitless) values. The **Built in** and default values are applicable to water. These parameters are used when calculating mobilities according to the **Debye-Hückel-Henry** relation in the species nodes.

In the **Water Self-Ionization** section you can change the default **Built in** expression for the **Water self-ionization constant**, pK_w (unitless), to any user defined expression.

Porous Matrix Properties

Use this node, available if **Mass transfer in porous media** has been enabled on the interface top-node, to define the **Porosity** (electrolyte volume fraction) and **Tortuosity** of a domain.

The porosity should be a number between 0 and 1.

Fully Dissociated Species

Use this node to define a fully dissociated charged species, such as strong bases and acids.

The **Charge number**, Z_0 (unitless), defines the species charge.

See also Common Settings for the Species Nodes in the Electrophoretic Transport Interface and Diffusion and Migration Settings.

Uncharged Species

Use this node to define a species that does not carry any charge, nor is impacted by the electric field.

See also Common Settings for the Species Nodes in the Electrophoretic Transport Interface and Diffusion and Migration Settings.

Weak Acid

The **Weak acid** node supports multiple dissociation steps, where the acid of the first dissociation step is uncharged.

The species may be either **Monoprotic,** subject to one dissociation step only, or **Polyprotic**. For the latter case any **Number of dissociation steps** larger than one may be used.

See also Common Settings for the Species Nodes in the Electrophoretic Transport Interface and Diffusion and Migration Settings.

Weak Base

The **Weak base** node supports multiple dissociation steps, where the base of the last dissociation step is uncharged.

The species may be either **Monoprotic,** subject to one dissociation step only, or **Polyprotic**. For the latter case any **Number of dissociation steps** larger than one may be used.

Note that the $\mathrm{p}K_a$ refers to the acid constant of the conjugate acid of the weak base.

See also Common Settings for the Species Nodes in the Electrophoretic Transport Interface and Diffusion and Migration Settings.

Ampholyte

Use the **Ampholyte** node generically to define any species where the average charge depends on the pH of the solution. The **Dissociation model** may be based either on a set of **Equilibrium constants** or an **Average charge**.

When using the **Equilibrium constants** the **Base charge in last dissociation step,** Z_0 (unitless), needs to be set.

The **Average charge**, $\bar{Z}$ (unitless) parameter is typically a function of pH and may be added as an analytical function or an interpolation polynomial under **Definitions**. The average squared charge, used in the electrolyte potential equation, is calculated automatically based on $\bar{Z}$.

See also Common Settings for the Species Nodes in the Electrophoretic Transport Interface and Diffusion and Migration Settings.

Protein

Use the **Protein** node to define macromolecules. The features of the Protein node are similar to the Ampholyte node, but with the default settings applicable for larger molecules.

See also Common Settings for the Species Nodes in the Electrophoretic Transport Interface and Diffusion and Migration Settings.

Current Source

To make this node available, click the **Show More Options** button ( ) and select **Advanced Physics Options** in the **Show More Options** dialog box.

Use this node to add a current source in a domain. A current source may appear in a domain in homogenized porous electrode modeling, but should normally not be used.

Initial Potential

Use this node to specify the **Initial Value** of the electrolyte potential for the solver.

Current

The **Current** boundary condition sets the total current or average current density over a boundary. It will set a constant electrolyte potential along the given boundary, which satisfies the current value setting.

This node is typically used to model electrode surfaces or boundaries facing an electrolyte reservoir (containing an electrode).

When using the **Total current** option in 1D or 2D, the boundary area is based either on the **Cross sectional area** (1D) or the **Out-of-Plane thickness** (2D) properties, set on the physics interface top node.

Current Density

Use the **Current Density** node to specify the current density distribution along a boundary.

This node is typically used to model electrode surfaces where the electrode kinetics depends on the electrolyte potential.

Note that using this node in 2D or 3D may result in an uneven potential distribution along the boundary. To mitigate such effects you may use the Current node instead.

Insulation

The **Insulation** boundary condition describes the walls of a cell or the boundaries of the cell that do not face an electrode (or a reservoir containing an electrode). The boundary condition imposes the following equation:

$$\mathbf{i}_l \cdot \mathbf{n} = 0$$

Potential

Add the **Potential** node on a boundary to set a fixed potential. This node is typically used to model electrode surfaces or boundaries facing an electrolyte reservoir.

The node sets the potential in the electrolyte, ϕ_l, to be equal to the **Boundary electrolyte potential,** $\phi_{l,\,\mathrm{bnd}}$ (SI unit: V).

CONSTRAINT SETTINGS

To display this section, click the **Show More Options** button ( ) and select **Advanced Physics Options** in the **Show More Options** dialog box.

Species Source

To make this node available, click the **Show More Options** button ( ) and select **Advanced Physics Options** in the **Show More Options** dialog box.

This node may be added as a subnode to any species node. See also Common Settings for the Species Nodes in the Electrophoretic Transport Interface.

In order to account for consumption or production of species, for example in porous electrodes or as a result of reversible reactions, the **Species Source** node adds source terms expressions S (SI unit: mol/(m^3·s) to the right-hand side of the transport equation of the parent species.

Initial Concentration

This node may be added as a subnode to any species node. See also Common Settings for the Species Nodes in the Electrophoretic Transport Interface.

This node specifies the initial value for the **Concentration**, c (mol/m^3), of the parent species. This value serve as the initial condition for a transient simulation. The value also serves as a start guess for stationary problems.

You can use spatially dependent functions (such as smoothed step functions) available under **Definitions** when defining the **Concentration** expression to specify different concentrations in different parts of the geometry. You can also use additional **Initial Values** node and modify the **Selection** to set different values for different domains.

Concentration

This node may be added as a subnode to any species node. See also Common Settings for the Species Nodes in the Electrophoretic Transport Interface

This condition node adds a boundary condition for the parent species concentration. Use the node to, for instance, specify the inlet concentration at the boundary facing a electrolyte reservoir.

No Flux

This node may be added as a subnode to any species node. See also Common Settings for the Species Nodes in the Electrophoretic Transport Interface.

This node is the default boundary condition on exterior boundaries. It represents boundaries where no mass flows in or out of the boundaries. Hence, the total flux is zero.

Flux

This node may be added as a subnode to any species node. See also Common Settings for the Species Nodes in the Electrophoretic Transport Interface.

This node can be used to specify the species inward flux across a boundary. The flux can represent a flux from or into a much larger surrounding environment, a phase change, or a flux due to chemical reactions.

INWARD FLUX

Enter a value or expression for the species mass flux J_0. Use a minus sign when specifying a flux directed out of the system.

External convection

Set **Flux type** to **External convection** to prescribe a flux to or from an exterior domain (not modeled) assumed to include convection. The exterior can for example include a forced convection to control the temperature or to increase the mass transport. In this case the prescribed mass flux corresponds to

$$J_0 = k_c(c_b - c)$$

where k_c is a mass transfer coefficient and c_b is the bulk concentration, the typical concentration far into the surrounding exterior domain.

Inflow

This node is available when you select the **Convection** check box on the physics interface **Settings** window.

Use this node to specify the species concentrations at an inlet boundary.

BOUNDARY CONDITION TYPE

The option **Concentration constraint** constrains the concentration values on the boundary by the use of pointwise constraints. When using this option the boundary condition is identical to the Concentration node.

The other option, **Flux (Danckwerts)** can be more stable and fast to solve when high reaction rates are anticipated in the vicinity of the inlet. Oscillations on the solutions can also be avoided in such cases. The latter condition uses a flux boundary condition based on the velocity across the boundary and the concentration values.

Outflow

Set this condition at outlets where species are transported out of the model domain by migration or fluid motion. It is assumed that migration and convection is the dominating transport mechanism across outflow boundaries, and therefore that diffusive transport can be ignored, that is:

$$\mathbf{n} \cdot (-D\nabla c) = 0$$

The Surface Reactions Interface

The **Surface Reactions (sr)** interface ( ), found under the **Chemical Species Transport** branch ( ) when adding a physics interface, is used to model the chemical reactions of surface and bulk species on a boundary. Surface species can be transported in the tangential direction of the surface by Fick's law whereas bulk species are assumed to be immobile on the surface.

The physics interface supports simulation of surface reactions on boundaries in 1D, 2D, and 3D as well as for axisymmetric components in 1D and 2D. The dependent variables are the surface concentrations, $c_{s,i}$ (SI unit: mol/m^2) and the bulk concentrations, $c_{b,i}$ (SI unit: mol/m^2).

When this physics interface is added, these default nodes are also added to the **Model Builder** — **Surface Properties**, **No Flux**, and **Initial Values**. Then, from the **Physics** toolbar, add other nodes that implement, for example, boundary conditions. You can also right-click **Surface Reactions** to select physics features from the context menu.

SETTINGS

The **Label** is the default physics interface name.

The **Name** is used primarily as a scope prefix for variables defined by the physics interface. Refer to such physics interface variables in expressions using the pattern `<name>.<variable_name>`. In order to distinguish between variables belonging to different physics interfaces, the `name` string must be unique. Only letters, numbers, and underscores (_) are permitted in the **Name** field. The first character must be a letter.

The default **Name** (for the first physics interface in the model) is `sr`.

DEPENDENT VARIABLES

Add or remove species and also change the names of the dependent variables that represent the species concentrations. Note that the names can be changed but the names of fields and dependent variables must be unique within a model.

Enter the **Number of surface species**. Use the **Add surface concentration** ( ) and **Remove surface concentration** ( ) buttons as needed. The same number of **Surface concentrations** `cs`, `cs2`, `cs3`, … are then listed in the table.

Enter the **Number of bulk species**. Use the **Add bulk concentration** (+) and **Remove bulk concentration** ( ) buttons as needed. The same number of **Bulk concentrations** `cb`, `cb2`, `cb3`, … are then listed in the table.

DISCRETIZATION

To display all settings available in this section, click the **Show More Options** button ( ) and select **Advanced Physics Options** in the **Show More Options** dialog box.

CONSISTENT AND INCONSISTENT STABILIZATION

To display these sections, click the **Show More Options** button ( ) and select **Stabilization** in the **Show More Options** dialog box.

By default the **Compensate for boundary stretching** check box is selected for the Surface Properties node. This section is then used to stabilize the tangential mesh velocity term.

When the **Compensate for boundary stretching** check box is cleared (not selected), and for fixed geometries or moving geometries, the stabilization has no effect.

See Surface Reaction Equations on Deforming Geometries for more information.

- Boundary, Edge, Point, and Pair Nodes for the Surface Reactions Interface
- Theory for the Surface Reactions Interface

Protein Adsorption: Application Library path **Chemical_Reaction_Engineering_Module/Mixing_and_Separation/protein_adsorption**

Boundary, Edge, Point, and Pair Nodes for the Surface Reactions Interface

The Surface Reactions Interface has these boundary, edge, point, and pair nodes, listed in alphabetical order, available from the **Physics** ribbon toolbar (Windows users),

Physics context menu (Mac or Linux users), or right-click to access the context menu (all users).

In general, to add a node, go to the **Physics** toolbar, no matter what operating system you are using.Subnodes are available by clicking the parent node and selecting it from the **Attributes** menu.

These nodes are described in this section:

- Initial Values
- Reactions
- Surface Concentration
- Surface Properties

All other available nodes are described for the Transport of Diluted Species interface. See Domain, Boundary, and Pair Nodes for the Transport of Diluted Species Interface.

In the *COMSOL Multiphysics Reference Manual* see Table 2-4 for links to common sections and Table 2-5 to common feature nodes. You can also search for information: press F1 to open the **Help** window or Ctrl+F1 to open the **Documentation** window.

Surface Properties

Use the **Surface Properties** node to define the density of sites, the site occupancy number, and the surface diffusion.

SPECIES CONSERVATION ON DEFORMING GEOMETRY

The **Compensate for boundary stretching** check box is selected by default. Click to clear the check box if required.

SITES

Enter a value or expression for the **Density of sites** Γ_s (SI unit: $\mathrm{mol/m^2}$). The default is 2×10^{-5} $\mathrm{mol/m^2}$.

Enter a **Site occupancy number** σ_i (dimensionless), indicating how many surface sites a surface species block upon adsorption.

This section is only present if the number of surface species is 1 or higher.

SURFACE DIFFUSION

Select a **Surface material** from the list. The default is **None**.

For each surface concentration species, the default **Diffusion coefficient** D_i (SI unit: m^2/s) is **User defined**. Select **Isotropic**, **Diagonal**, **Symmetric**, or **Full** depending on the characteristics of the surface, and then enter values or expressions in the field or matrix.

This section is only present if the number of surface species is 1 or higher.

BULK SPECIES

For each bulk species enter the **Molar mass** M_i (SI unit: kg/mol) and the **Density** ρ_i (SI unit: kg/m^3). The default molar mass is 0.144 kg/mol and the default density is 5320 kg/m^3).

This section is only present if the number of bulk species is 1 or higher.

Surface Reaction Equations on Deforming Geometries

Initial Values

The **Initial Values** node allows the initial value or guess for the surface and bulk concentrations.

INITIAL VALUES

Based on the number of surface species and number of bulk species entered for the physics interface under Dependent Variables section, enter values for the same number of **Surface concentration** `cs`, `cs2`, `cs3`, … (SI unit: mol/m^2) and **Bulk concentration** `cb`, `cb2`, `cb3`, … (SI unit: mol/m^2) in each field.

Reactions

The **Reactions** node adds rate expression terms to the species transport equations in order to account for consumption or production of species due to reactions.

REACTION RATE FOR SURFACE SPECIES

Add a reaction rate expression, $R_{s,cs1,cs2...}$ (SI unit: $mol/(m^2 \cdot s)$), for each surface species taking part in a surface reaction.

This section is only present if the number of surface species is 1 or higher.

REACTION RATE FOR BULK SPECIES

Add a reaction rate expression, $R_{b,\mathrm{cb1,cb2...}}$ (SI unit: mol/(m^2·s)), for each bulk species taking part in a surface reaction.

This section is only present if the number of bulk species is 1 or higher.

Surface Concentration

Use the **Surface Concentration** node to set the surface concentrations for one or more species on an edge (3D components) or a point (2D and 2D axisymmetric components).

SURFACE CONCENTRATION

Select each species check box as needed and enter a value or expression for each species concentration, $c_{\mathrm{s,0,cs1,cs2...}}$ (SI unit: mol/(m^2·s)).

CONSTRAINT SETTINGS

To display this section, click the **Show More Options** button ( ) and select **Advanced Physics Options** in the **Show More Options** dialog box.

The Reacting Flow Multiphysics Interface

Reacting Flow is a predefined multiphysics interface, available in the Chemical Reaction Engineering Module, that couples fluid flow with mass transport and reactions.

Selecting **Laminar Flow** under the **Chemical Species Transport>Reacting Flow** branch of the **Model Wizard** or **Add Physics** windows, a **Laminar Flow** interface and a **Transport of Concentrated Species** interface are added to the Model Builder.

In addition, the Multiphysics node is added, which includes the multiphysics coupling feature **Reacting Flow**. The **Reacting Flow** feature predefines and controls the couplings between the separate interfaces in order to facilitate easy set up of models.

In this section:

- The Reacting Laminar Flow Interface
- The Reacting Flow Coupling Feature
- Physics Interface Features

The Reacting Laminar Flow Interface

The **Reacting Laminar Flow** multiphysics interface is used to simulate laminar flow coupled to species transport in a gas or liquid.

It combines the **Laminar Flow**, and **Transport of Concentrated Species** interfaces. The **Reacting Flow** multiphysics coupling, which is added automatically, couples fluid flow and mass transport. The fluid flow can either be free flow or flow in a porous medium. The species transport supports both a mixture, where the concentrations are of comparable order of magnitude, and low-concentration solutes in a solvent.

The interface can be used for stationary and time-dependent analysis in 2D, 2D axial symmetry, and 3D.

On the constituent physics interfaces:

The equations solved by the **Laminar Flow** interface are the Navier-Stokes equations for conservation of momentum and the continuity equation for conservation of mass. A **Fluid Properties** feature is active by default on the entire interface selection. A **Fluid and**

Matrix Properties feature can be added in order to model flow in porous media by solving the Brinkman equations.

The **Transport of Concentrated Species** interface solves for an arbitrary number of mass fractions. The species equations include transport by convection, diffusion and, optionally, migration in an electric field.

The **Reacting Laminar Flow** interface triggers pseudo time stepping for the flow equations when **Use pseudo time stepping for stationary equation form** in the **Fluid Flow** interface is set to **Automatic from physics**.

The Reacting Flow Coupling Feature

Use the **Reacting Flow** ( ) multiphysics coupling to simulate mass transport and reactions in a gas or liquid mixture where the fluid flow can be dependent on the mixture composition.

DOMAIN LEVEL SYNCHRONIZATION

The **Reacting Flow** coupling synchronizes the features from a Single-Phase Flow, or Brinkman Equations, interface and a Transport of Concentrated Species interface. When added, the density in the Single-Phase Flow interface is automatically synchronized to the one defined by the Transport of Concentrated Species interface. Conversely, the velocity field used by the latter interface is synchronized to the one computed in the former interface.

THE STEFAN VELOCITY

The **Reacting Flow** coupling feature automatically couples mass transfer on boundaries and applies a corresponding velocity contribution for the flow. Prescribing a net mass boundary flux in the **Transport of Concentrated Species** interface, either using a **Flux** or **Mass Fraction** feature, the **Reacting Flow** feature computes The Stefan Velocity and applies this in **Wall** features using the same selection.

MASS TRANSFER TO OTHER PHASES IN POROUS MEDIA

When coupled to the **Brinkman Equations** interface, the **Reacting Flow** node automatically computes the net mass source or sink in a **Reactions** (when **Mass transfer to other phases is enabled**) node in the **Transport of Concentrated Species** interface and adds the corresponding source/sink to the momentum equations of the **Fluid and Matrix Properties** domains.

SETTINGS

The **Label** is the default multiphysics coupling feature name.

The **Name** is used primarily as a scope prefix for variables defined by the coupling node. Refer to such variables in expressions using the pattern `<name>.<variable_name>`. In order to distinguish between variables belonging to different coupling nodes or physics interfaces, the `name` string must be unique. Only letters, numbers, and underscores (_) are permitted in the **Name** field. The first character must be a letter.

The default **Name** (for the first multiphysics coupling feature in the model) is `rf1`.

DOMAIN SELECTION

The **Reacting Flow** coupling is automatically defined on the intersection of the selections for the coupled interfaces.

The **Selection** list displays the domains where the coupling feature is active.

COUPLED INTERFACES

This section defines the physics involved in the multiphysics coupling. The **Fluid flow** and **Species transport** lists include all applicable physics interfaces.

The default values depend on how this coupling node is created.

- If it is added from the **Physics** ribbon (Windows users), **Physics** contextual toolbar (Mac and Linux users), or context menu (all users), then the first physics interface of each type in the component is selected as the default.
- If it is added automatically when a multiphysics interface is chosen in the **Model Wizard** or **Add Physics** window, then the two participating physics interfaces are selected.

You can also select **None** from either list to uncouple the node from a physics interface. If the physics interface is removed from the **Model Builder**, for example **Laminar Flow** is deleted, then the **Species transport** list defaults to **None** as there is nothing to couple to.

Click the **Go to Source** buttons ( ) to move to the main physics interface node for the selected physics interface.

Click the **Show or Hide Physics Properties Settings** button ( ) to toggle the display of physics properties settings affecting the coupling feature. When a turbulence model is used, turbulent mass transfer is automatically accounted for (see the settings in the **Turbulence** section below). Using Reacting Flow, the mass transfer treatment at walls follows that applied for the fluid flow. Therefore the **Wall treatment** setting is also displayed when using a turbulence model. For more information on turbulent mass

transfer at walls, see the section Mass Transport Wall Functions in the *CFD Module User's Guide*.

If a physics interface is deleted and then added to the model again, then in order to reestablish the coupling, you need to choose the physics interface again from the **Fluid flow** or **Species transport** lists. This is applicable to all multiphysics coupling nodes that would normally default to the once present interface. See Multiphysics Modeling Workflow in the *COMSOL Multiphysics Reference Manual*.

TURBULENCE

When the fluid flow interface uses a turbulence model, select an option from the **Mass transport turbulence model** list — **Kays-Crawford**, **High Schmidt Number**, or **User-defined turbulent Schmidt number**.

For **User-defined turbulent Schmidt number**, enter a **Turbulent Schmidt number** Sc_T (dimensionless).

The turbulent mass transfer added to the mass fraction equations is defined as

$$N_{i,\mathrm{T}} = -\frac{\mu_\mathrm{T}}{\mathrm{Sc}_\mathrm{T}}\nabla\omega_i$$

where μ_T is the turbulent viscosity defined by the flow interface, and the turbulent Schmidt number, Sc_T, depends on the **Mass transport turbulence model** used.

Note, since the **Reacting Flow** coupling feature adds the turbulent mass transport, it should not be combined with a **Turbulent Mixing** feature (subfeature to **Transport Properties** in the **Transport of Concentrated Species interface**).

Physics Interface Features

Physics nodes are available from the **Physics** ribbon toolbar (Windows users), **Physics** context menu (Mac or Linux users), or right-click to access the context menu (all users).

In general, to add a node, go to the **Physics** toolbar, no matter what operating system you are using.

LAMINAR FLOW

The available physics features for The Laminar Flow interface are listed in the section Domain, Boundary, Pair, and Point Nodes for Single-Phase Flow in the *COMSOL Multiphysics Reference Manual*.

TRANSPORT OF CONCENTRATED SPECIES

The available physics features for The Transport of Concentrated Species interface are listed in the section Domain, Boundary, and Pair Nodes for the Transport of Concentrated Species Interface.

The Reacting Flow in Porous Media Multiphysics Interface

The Chemical Reaction Engineering Module includes two predefined multiphysics interface that couples fluid flow in porous media with mass transport and reactions in porous media.

Selecting a multiphysics interface under the **Chemical Species Transport>Reacting Flow in Porous Media** branch of the **Model Wizard** or **Add Physics** windows, a **Brinkman Equations** interface combined with either the **Transport of Diluted Species in Porous Media** interface or the **Transport of Concentrated Species** interfaces are added to the Model Builder.

In addition, the Multiphysics node is added, which includes the multiphysics coupling feature. The multiphysics coupling feature controls the coupling between the separate interfaces in order to facilitate easy setup of models.

In this section:

- The Reacting Flow in Porous Media, Transport of Diluted Species Interface
- The Reacting Flow in Porous Media, Transport of Concentrated Species Interface
- The Reacting Flow, Diluted Species Coupling Feature
- The Reacting Flow Coupling Feature
- Physics Interface Features

The Reacting Flow in Porous Media, Transport of Diluted Species Interface

The **Reacting Flow in Porous Media, Transport of Diluted Species** interface ( ) is used to study the flow and chemical composition of a gas or liquid moving through the interstices of a porous medium.

It combines the **Brinkman Equations**, and **Transport of Diluted Species in Porous Media** interfaces. The **Reacting Flow, Diluted Species** multiphysics coupling feature, which is added automatically, couples the fluid flow and mass transport.

The interface can be used for stationary and time-dependent analysis in 2D, 2Daxi and 3D.

On the constituent physics interfaces:

The **Brinkman Equations** interface computes the fluid velocity and pressure fields of single-phase flow in porous media in the laminar flow regime. A **Fluid and Matrix Properties** feature is active by default on the entire interface selection.

The **Transport of Diluted Species in Porous Media** interface computes the species concentration in free and porous media, assuming that the species are of solutes, dissolved in a solvent of significantly higher concentration. The species equations include transport by convection, diffusion and, optionally, migration in an electric field.

The Reacting Flow in Porous Media, Transport of Concentrated Species Interface

The **Reacting Flow in Porous Media, Transport of Concentrated Species** interface ( ) is used to study the flow and chemical composition of a gas or liquid moving through the interstices of a porous medium. The fluid can consist of a mixture of species where the individual concentrations are of comparable order of magnitude.

It combines the **Brinkman Equations**, and **Transport of Concentrated Species** interfaces. The **Reacting Flow** multiphysics coupling feature, which is added automatically, couples the fluid flow and mass transport.

The interface can be used for stationary and time-dependent analysis in 2D, 2Daxi and 3D.

On the constituent physics interfaces:

The **Brinkman Equations** interface computes the fluid velocity and pressure fields of single-phase flow in porous media in the laminar flow regime. A **Fluid and Matrix Properties** feature is active by default on the entire interface selection.

The **Transport of Concentrated Species** interface solves for an arbitrary number of mass fractions in free and porous media. In the current multiphysics interface a **Porous Media Transport Properties** feature is active by default on the entire interface selection.

The Reacting Flow, Diluted Species Coupling Feature

For the settings of this feature see The Reacting Flow, Diluted Species Coupling Feature in the *COMSOL Multiphysics Reference Manual*.

The Reacting Flow Coupling Feature

For the settings of this feature see The Reacting Flow Coupling Feature.

Physics Interface Features

Physics nodes are available from the **Physics** ribbon toolbar (Windows users), **Physics** context menu (Mac or Linux users), or right-click to access the context menu (all users).

BRINKMAN EQUATIONS

The available physics features for The Brinkman Equations interface are listed in the Domain, Boundary, Point, and Pair Nodes for the Brinkman Equations Interface section in the *CFD Module User's Guide*.

TRANSPORT OF DILUTED SPECIES

The available physics features for The Transport of Diluted Species interface are listed in the Domain, Boundary, and Pair Nodes for the Transport of Diluted Species Interface section.

TRANSPORT OF CONCENTRATED SPECIES

The available physics features for The Transport of Concentrated Species interface are listed in the Domain, Boundary, and Pair Nodes for the Transport of Concentrated Species Interface section.

4

Fluid Flow Interfaces

The functionality for simulating fluid flow in free, porous media is found under the **Fluid Flow** branch ( ) when adding a physics interface.

The documentation of the available interfaces and features can be found in *CFD Module User's Guide* in the chapters Single-Phase Flow Interfaces and Porous Media and Subsurface Flow Interfaces.

Modeling Fluid Flow

In this section:

- Available Physics Interfaces
- Coupling to Other Physics Interfaces

Available Physics Interfaces

This module primarily models the transport and conversion of mass in chemical reactors and other reacting systems. Many of these applications include transport through convection, and the module includes a number of physics interfaces for the simulation of fluid flow, particularly within porous media. As with all other physical descriptions simulated by COMSOL Multiphysics, any description of fluid flow can be directly coupled to any other physical process. This is particularly relevant for systems based on turbulent or multiphase flow, which are supported by the CFD Module. For detailed descriptions of the fluid-flow interfaces listed below, see the *CFD Module User's Guide*.

The **Fluid Flow** branch ( ) has a number of subbranches to describe momentum transport. The Laminar Flow Interface ( ), found under the **Single-Phase Flow** branch ( ) when adding a physics interface, is used to model laminar flow described by the Navier-Stokes equations. It is also possible to extend this physics interface to study nonisothermal or non-Newtonian flow.

The Creeping Flow Interface ( ), also under the **Single-Phase Flow** branch ( ), is used to model flow fluid flows at very low Reynolds numbers, also referred to as Stokes flow. This typically occurs in fluid systems with high viscosity or small geometrical length scales (for example in microfluidics and MEMS devices).

The rest of the available physics interfaces for fluid flow are found under the **Porous Media and Subsurface Flow** branch ( ).

The Darcy's Law Interface ( ) is used to model fluid movement through interstices in a porous medium where a homogenization of the porous and fluid media into a single medium is done. This physics interface combines the continuity equation and an equation of state for the pore fluid (or gas), can be used to model low velocity flows, for which the pressure gradient is the major driving force.

Darcy's law can be used in porous media where the fluid is mostly influenced by the frictional resistance within the pores. When the size of the interstices are larger and the fluid is influenced by itself, the kinetic potential from fluid velocity, pressure, and gravity must be also be considered, and The Brinkman Equations Interface ( ) is the appropriate physics interface to use.

The Brinkman equations extend Darcy's law to describe the dissipation of the kinetic energy by viscous shear, similar to the Navier-Stokes equation. Consequently, they are well suited to transitions between slow flow in porous media, governed by Darcy's law, and fast flow in channels described by the Navier-Stokes equations. The equations and boundary conditions that describe these types of phenomena are also found in The Free and Porous Media Flow Interface ( ).

The next section briefly discusses coupling to other physics interfaces.

Coupling to Other Physics Interfaces

Often, you are simulating applications that couple fluid flow in free porous media to another type of phenomenon described in another physics interface. This can include chemical reactions and mass transport, as covered in the Chemical Species Transport branch, or energy transport in porous media found in the Heat Transfer branch.

More advanced descriptions of fluid flow, such as turbulent and multiphase flow, can be found in the CFD Module. More extensive descriptions of heat transfer, such as that in turbulent flow or systems including radiation, can be found in the Heat Transfer Module. Furthermore, some applications that involve electrochemical reactions and porous electrodes, particularly in electrochemical power source applications, are better handled by the Battery Design Module.

5

Heat Transfer Interfaces

The functionality for simulating heat transfer in free and porous media is found under the **Heat Transfer** branch ( ) when adding a physics interface.

The documentation of all features in the Heat Transfer in Porous Media interface can be found in the *Heat Transfer Module User's Guide*, in the chapter Heat Transfer Interfaces.

Modeling Heat Transfer

Available Physics Interfaces

Heat transfer is an important part of chemical reaction engineering. Most chemical reactions either require or produce heat, which in turn affects both the reactions themselves and other physical processes connected to the system.

The heat transfer branch includes a number of physics interfaces for the simulation of heat transfer, particularly in porous media. As with all other physical descriptions simulated by COMSOL Multiphysics, any description of heat transfer can be directly coupled to any other physical process. This is particularly important for systems based on chemical reactions and mass transfer, along with fluid flow.

You can manipulate these physics interfaces with respect to including source and sink terms or, in other words, account for exothermic or endothermic chemical reactions.

If you also have the Heat Transfer Module there are additional Heat Transfer interface features, such as radiation, available.

Coupling Heat Transfer with Other Physics Interfaces

The Reaction Engineering Interface includes support for setting up and simulating chemical reactions, including reaction kinetics through the temperature-dependent Arrhenius expression and mass action law. This physics interface also has support for including and calculating thermodynamic data as temperature-dependent expressions. The Reaction Engineering interface can generate a space-dependent model using any heat transfer interface to benefit from the bidirectional dependence between heat transfer and chemical reactions.

More advanced descriptions of fluid flow, such as turbulent and multiphase flow, require the CFD Module. In addition, the Heat Transfer Module also includes more detailed descriptions and tools for simulating energy transport, such as radiation.

6

Thermodynamics

This chapter describes how you can use the thermodynamics functionality to define thermo-physical and transport properties. The properties in turn can be used when simulating chemical reaction systems, or any type of transport model involving mass transfer, fluid flow, or heat transfer.

In this chapter:

- Using Thermodynamic Properties
- Thermodynamic Models and Theory

Using Thermodynamic Properties

In this section:

- Workflow for Thermodynamics Property Calculations
- Thermodynamics
- Thermodynamic System
- External Thermodynamic Packages
- External Thermodynamic System
- Predefined System
- Exporting and Importing Thermodynamic Systems
- Species Property
- Mixture Property
- Equilibrium Calculation
- Generate Chemistry
- Generate Material
- Coupling with the Reaction Engineering and the Chemistry Interfaces
- Evaluating a Property Function in a Physics Interface
- User-Defined Species
- References

Workflow for Thermodynamics Property Calculations

The thermodynamic properties database, together with the thermodynamic calculator, make it possible to evaluate physical properties of fluids such as heat capacity, thermal conductivity, density and diffusivity, as well as equilibrium compositions of two phases at equilibrium. The properties can be calculated for pure fluids, mixtures, and for two-phase fluid systems consisting of pure species as well as mixtures.

Using the thermodynamics functionality involves the following main steps:

1 Add the **Thermodynamics** node and create a thermodynamic system to add properties for a selected set of chemical compounds, referred to as chemical species in this manual. A thermodynamic system can be created in the following ways:

- A built-in **Thermodynamic System** uses the built-in, or user-defined, property database with native functionality for thermodynamic property calculations.
- An **External Thermodynamic System** uses properties from an installed external package provider. For more information on how to enable the use of external packages see the Installing External Thermodynamic Packages — An Example.
- A **Predefined System** uses the built-in database with native functionality to set up one of the following common systems; Dry air, Moist air, or Water-steam.

2 Once a thermodynamic system is set up, it can be used to define a multitude of property functions. The Generate Material option provides a fast route to defining the material properties most commonly required for fluid flow, heat transfer and mass transfer modeling. By specifying the composition and phase of the mixture, a **Material** node can automatically be set up. The material node can include properties such as density, heat capacity, heat capacity ratio, thermal conductivity and viscosity.

3 Users of the Reaction Engineering, or Chemistry interface can couple chemical species in these interfaces with the chemical species in the thermodynamic system. When Coupling with the Reaction Engineering and the Chemistry Interfaces the required property parameters and functions are automatically added and visualized as nodes under the corresponding thermodynamic system node.

4 As an alternative to the functions automatically set up when using Generate Material or coupling to e.g. Chemistry, functions or constants can be set up manually for any thermodynamic system. This is accomplished using the thermodynamic features Species Property, Mixture Property or Equilibrium Calculation. You can, for example, create a **Species Property** function describing the density of a fluid, and use this function in a fluid-flow interface. With **Mixture Property** you can define mixture functions, i.e. functions that depend on the composition of a mixture, describing for example density, enthalpy, or heat capacity.

The functionalities described in Step 2- 4 generate functions and constants, defined by a thermodynamic system, that can be used in any physics interface in COMSOL Multiphysics. The functions are used to evaluate fluid properties that depend on variables such as temperature, pressure, and mixture composition. For more information, see Evaluating a Property Function in a Physics Interface.

Thermodynamics

To access the functionality for thermodynamic calculations, right-click the **Global Definitions** node in the **Model Builder** tree and select **Thermodynamics** ( ). Using the Reaction Engineering or Chemistry interfaces, **Thermodynamics** is also available on the **Reaction Engineering** or **Chemistry** toolbar.

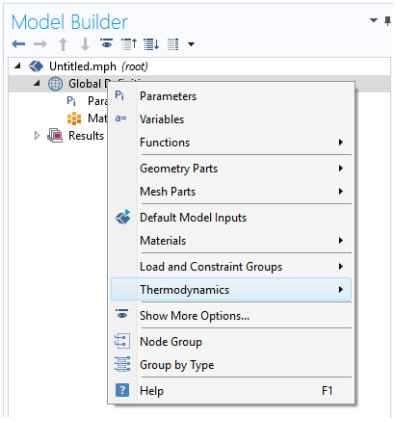


Figure 6-1: The Thermodynamics feature available under Global Definitions.

Thermodynamic properties given as parameters or functions are collected in a so called thermodynamic system. Each thermodynamic system includes a set of available species and phases, as well as different models used for the thermodynamic property calculations, for example an equation of state such as Peng-Robinson.

Select Thermodynamic System in the context menu to add a thermodynamic system that uses the database included in the Liquid & Gas Properties Module.

As an alternative, selecting External Thermodynamic System can make use of an installed thermodynamics software to make the corresponding calculations.

The option Predefined System, allows you to set up one of the following systems; Dry air, Moist air, or Water-steam.

It is also possible to import previously created and stored thermodynamic systems by selecting **Import Thermodynamic System** (see Exporting and Importing Thermodynamic Systems).

In addition to creating thermodynamic systems, you can also define User-Defined Species in Thermodynamics. Use **User-Defined Species** to add new species that are not available in COMSOL database. You can also edit available species in the database.

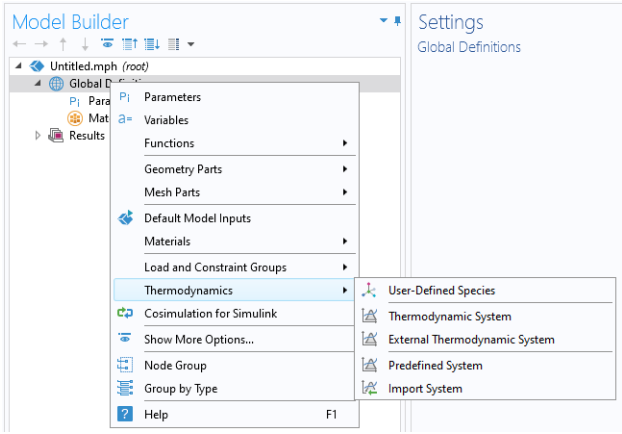


Figure 6-2: Adding Thermodynamic Systems to the Thermodynamics node. Note that external package providers have been installed.

When a thermodynamic system has been added, thermodynamic and transport properties are defined by functions. These can be used to describe properties for pure species, mixtures, and for gas-liquid (or liquid-liquid) systems at equilibrium.

Thermodynamic System

A thermodynamic system is used to describe properties of pure species and mixtures of chemical compounds for liquids, gases, liquid-vapor equilibria, and liquid-liquid equilibria. It specifies the available species and the phases (states of aggregation) that are present in the modeled system. It also defines and evaluates the functions for thermodynamic and transport properties of the chemical system, that is, the species and mixture properties for liquids, gases and phase equilibria.

To create a **Thermodynamic System**, start the **Thermodynamic System Wizard** in one of the following ways:

- Right-click the **Global Definitions** node, select **Thermodynamics** and choose **Thermodynamic System**.
- Using the Reaction Engineering interface, choose **Thermodynamic System** from the **Thermodynamics** section of the **Reaction Engineering** toolbar.
- Correspondingly, using the Chemistry interface, choose **Thermodynamic System** from the **Thermodynamics** section of the **Chemistry** toolbar.

The **Thermodynamic System Wizard** contains the following steps:

1 Select System

2 Select Species

3 Select Thermodynamic Model

SELECT SYSTEM

Use the **Select System** step in the wizard to define the phases in the modeled system. You can select **Gas**, **Liquid**, **Vapor-liquid**, **Vapor-liquid-liquid**, or **Liquid-liquid**. The names of the phases in the Selected system table can be changed by editing the element in the Name column. Click the **Next** button ( ) to proceed to the next step in the wizard.

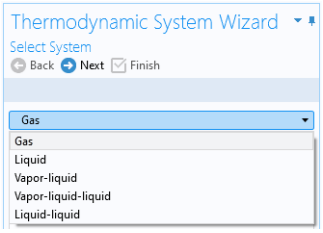


Figure 6-3: Thermodynamic System Wizard: Select System.

SELECT SPECIES

Use the **Species** Type filter text field to search among the available species in the **COMSOL** database or the User-Defined Species. Species can be searched for by typing the name, CAS number, or the chemical formula. Select one or more species in the list and click the **Add Selected** button ( ) to add species to the **Selected species** table. To remove species from the Selected species table, use either the Remove Selected button ( )

or the Remove All button ( ), both located below the table. Click the **Next** button ( ) to proceed to the next step in the wizard.

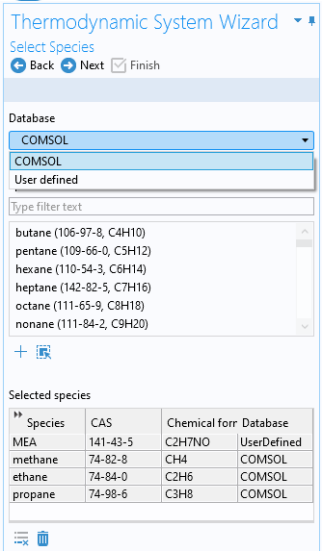


Figure 6-4: Thermodynamic System Wizard: Select Species.

SELECT THERMODYNAMIC MODEL

The Thermodynamic model controls the relations between the intensive thermodynamic properties of the system such as pressure, specific volume, and temperature. It also controls how extensive properties like enthalpy, entropy, or the heat capacity of the system are computed. Furthermore, the Thermodynamic model specifies the default models used to compute transport properties.

The following Thermodynamic Models are available for all phases:

- Peng-Robinson
- Peng-Robinson (Twu)
- Soave-Redlich-Kwong
- Soave-Redlich-Kwong (Graboski-Daubert)

For a system including only gas phase, or for liquid phase systems with thermodynamic models requiring an equation of state, the Ideal Gas Law is added to the available models in the **Gas phase model** list or **Equation of state** list.

When the system includes one or more liquid phases, the following additional models are also available (in the **Liquid phase model** list):

- Chao Seader (Grayson-Streed)
- Wilson
- NRTL
- UNIFAC VLE
- UNIQUAC
- Regular Solution
- Extended Regular Solution
- Ideal Solution

These models correspond to activity models.

To calculate properties of water and steam, use the Water (IAPWS) model. This is available for systems that include a single water species.

For recommendations regarding the appropriate thermodynamic model, based on the available phases and the system pressure level, see the section Selecting the Right Thermodynamic Model.

Select the **Advanced options** check box in order to manually control the models used for thermodynamic properties, transport properties, and surface tension. When this check box is selected, all available property models are shown in the property model table. The available property models are dependent on the phases available in the thermodynamic system.

When only a gas phase is present, models are available for the following properties:

- Gas diffusivity
- Gas thermal conductivity
- Gas viscosity

For a single-phase liquid, or for a two-phase liquid-liquid system, there are models for the following properties:

- Liquid diffusivity
- Liquid diffusivity at infinite dilution
- Liquid-liquid surface tension
- Liquid thermal conductivity

- Liquid viscosity
- Liquid volume

For systems with both vapor and liquid phases, all of the above properties are available, as well as Gas-liquid surface tension.

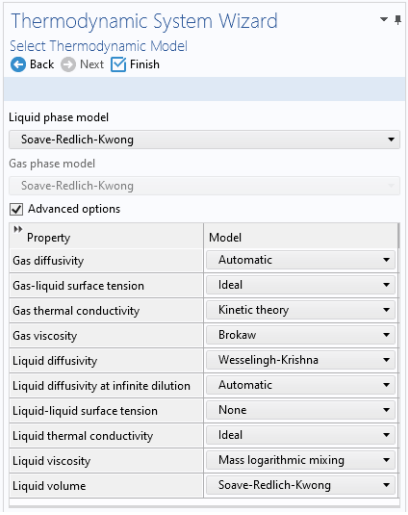


Figure 6-5: Thermodynamic System Wizard: Advanced thermodynamic model options available for a Vapor-liquid system.

Click the **Finish** button ( ) to exit the **Thermodynamic System Wizard** and add the corresponding system under the **Thermodynamics** node. Note that the default node label reflects the available phase in the system. For example, when creating a vapor-liquid system, a node labeled **Vapor-Liquid System** is added. The name of the system can be changed using the Label text field in the Settings window for the system.

SETTINGS

Selecting a Thermodynamic System or Predefined System node shows its **Settings** window with a description of the package content and the available properties. Editing

the text in the Label text field changes the name of the system. Below follows a description of the thermodynamic system settings.

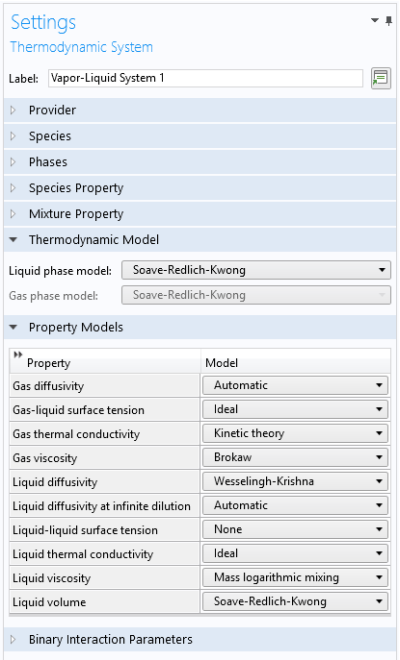


Figure 6-6: Thermodynamic System Settings.

Provider:
Contains information about the thermodynamic system such as the version it was created in and the manager used to create it. For a built-in thermodynamic system, the manager corresponds to COMSOL.

Species:
Lists the species included in the thermodynamic system. You can change the list of species by right-clicking the **Thermodynamic System** node and selecting Add or Remove Species.

Phases:
Lists the phases included in the thermodynamic system. You can add or remove phases, such as gas, liquid or liquid-vapor, by right-clicking the **Thermodynamic System** node and selecting Define System.

Species Property:
Lists the parameters and functions that describe thermodynamics and transport properties for pure species. Such functions may describe density, heat capacity, thermal conductivity, or other thermodynamic and transport properties. For more information, see Species Property.

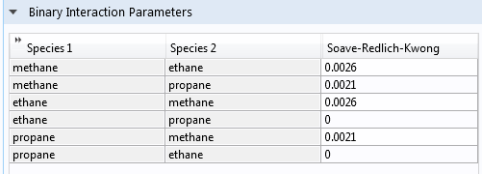
Mixture Property:
Lists the available mixture property functions. Note that you have to have a mixture model defined in order to use these functions. You can define a mixture property by right-clicking the **Thermodynamic System** node and selecting Mixture Property.

Thermodynamic Model:
When a liquid is present, use the **Liquid phase model** list to select the thermodynamic model for this phase.

When a gas is present, use the **Gas phase model** list to select the thermodynamic model for this phase. If also a liquid phase is available, and the **Liquid phase model** corresponds to an equation of state, then the **Gas phase model** is set to the same model.

Property Models:
Displays the settings for the available individual property models. The property models can be changed by selecting different values from the combo box in the Model column. For example, for **Gas thermal conductivity** you can select **Kinetic theory** or **Ideal** from the corresponding combo box. You can also select the property model in the last step of the thermodynamic system wizard by selecting the **Advanced option** check box, see Select Thermodynamic Model.

Binary Interaction Parameters:
This section can be used to inspect and edit binary interaction parameters. Select a pair of species (first and second column, Species 1 and Species 2) as shown in Figure 6-7 to edit the corresponding binary interaction parameter currently in use. In cases that the thermodynamic model has more than one type of binary interaction parameter, each type of the interaction parameter will be shown in a column in the table.


Binary Interaction Parameters

Species 1	Species 2	Soave-Redlich-Kwong
methane	ethane	0.0026
methane	propane	0.0021
ethane	methane	0.0026
ethane	propane	0
propane	methane	0.0021
propane	ethane	0

Figure 6-7: Entering the Binary Interaction Parameters for the Soave-Redlich-Kwong model.

When a binary interaction parameter is not available in the database for a pair of species, the parameter value is set to zero (default value).

MODIFYING AN EXISTING SYSTEM

It is possible to modify an existing thermodynamic system, for example by changing the included species or phases. To do so, right-click the **Thermodynamic System** node and select Add or Remove Species, or Define System from the context menu. Both of these options are available for systems created using Thermodynamic System. For a **Predefined System**, the option **Add or Remove Species** is available for Dry Air and Moist Air. For a Water-steam system, neither of the two options are available.

When the properties of a User-Defined Species has been changed, select Update From Species for the changes to take effect in the thermodynamic system.

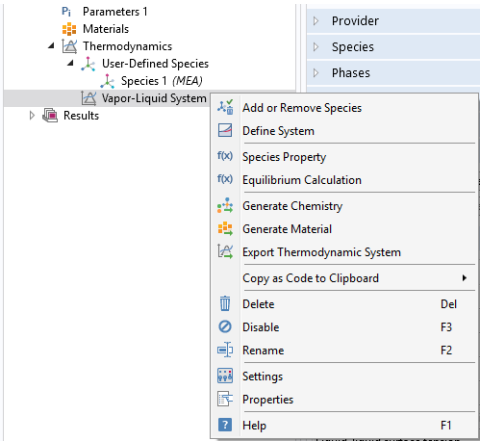


Figure 6-8: Modifying the species and phases of a thermodynamic system.

Add or Remove Species

Selecting **Add or Remove Species** takes you to the Select Species step in the **Thermodynamic System Wizard**. Use the **Add Species** button ( ) to add a species to the **Selected Species** list. To remove a species, select it in the list and use the **Remove Species** button ( ).

Make sure to click the **Finish** button ( ) in order for the changes to take effect.

Note that adding or removing species in a thermodynamic system that is currently coupled to a Reaction Engineering interface or a Chemistry interface breaks this coupling. See the Coupling with the Reaction Engineering and the Chemistry Interfaces for how to update this coupling.

Define System

Selecting **Define System** takes you to the Select System step in the **Thermodynamic System Wizard**. You can select the desired system from the list.

Make sure to click the **Finish** button ( ) button in order for the changes to take effect.

Note that changing the phase(s) in a thermodynamic system that is currently coupled to a Reaction Engineering interface or a Chemistry interface breaks this coupling. See the Coupling with the Reaction Engineering and the Chemistry Interfaces section for how this coupling can be updated.

Update From Species

This option is available in a **Thermodynamic System** that includes a User-Defined Species. Use it to update the system following a change in the species properties.

WARNING INFORMATION

A sanity check is always performed when a **Thermodynamic System** is created. If any problems are found, a Warning Information node listing the problems is added under the package. One example when this occurs is when a parameter required for the thermodynamic model, typically a binary interaction parameter, is not available in the database.

External Thermodynamic Packages

The thermodynamics functionality includes support for creating properties from external thermodynamic packages. In order to use external packages, the external software has to be CAPE-OPEN compliant. The Liquid & Gas Properties Module supports the CAPE-OPEN Thermo 1.1 and the CAPE-OPEN Thermo 1.0 standards.

CAPE-OPEN is an open interface standard for chemical process simulation software (Ref. 1). This standard defines rules and interfaces that allows linking between compliant software. Some examples of CAPE-OPEN compliant software are:

- COCO/TEA (Free of charge package provider; see Ref. 2).
- Multiflash™ (KBC Advanced Technologies plc).
- VMGThermo™ (Virtual Materials Group, Inc.).
- Simulis® Thermodynamics (ProsSim SA).
- Aspen Properties, aspenONE® (Aspen Technology, Inc.).
- COMThermo® packages (comes with Aspen HYSYS®).

Accessing external thermodynamic systems allows species properties, mixture properties, as well as phases equilibrium calculations (gas-vapor, liquid-liquid) to be obtained from external software, such as the ones listed above.

INSTALLING EXTERNAL THERMODYNAMIC PACKAGES — AN EXAMPLE

TEA is a thermodynamics thermodynamic system that handles the physical and thermodynamic property calculations for the simulation environment COCO. The property data bank contains of over 190 commonly used chemicals, and the package exhibits more than 100 property calculation routines with their analytical or numerical derivatives. COCO is maintained by AmsterCHEM and is free to download from the Internet (Ref. 2).

To use the external physical and thermodynamic property calculations from COCO/TEA in COMSOL Multiphysics models, you need to go through the following steps:

1. Download and install COCO, which includes the TEA thermodynamic system manager. The software is available from www.cocosimulator.org/index_download.html.
2. Create and configure a thermodynamic system template that handles physical and thermodynamics calculations needed for your model. If you have already created a package template earlier, or if an adequate thermodynamic system already exists in the installation, this step is not needed.
3. Create an External Thermodynamic System node as detailed in the next section. The installed packages are available in the Select Property Package step of the Thermodynamic System Wizard.

External Thermodynamic System

The following assumes that you have installed external thermodynamic packages from a CAPE-OPEN compliant software in the manner outlined in Installing External Thermodynamic Packages — An Example.

Locate the **Thermodynamics** node and right-click to add an **External Thermodynamic System** (Figure 6-2). Using a **Reaction Engineering** or **Chemistry** interface, you can also add an external package by choosing **External Thermodynamic System** from the **Thermodynamics** section of the **Reaction Engineering,** or **Chemistry,** toolbar.

SELECT PROPERTY PACKAGE

All installed packages, from providers such as COCO/TEA, Aspen Properties, etc, are available in the **Thermodynamic System Wizard** (Figure 6-9). Select one of the packages and click the **Finish** button ( ) in the upper right corner of the wizard in order to add the package as an **External Thermodynamic System** node under the **Thermodynamics** node.

When adding the package its default label reflects the included phases. For example, a node labeled **Vapor-Liquid System (External)** is created when adding an external package containing a vapor and a liquid phase. The name of the system can be changed using the Label text field in the Settings window for the system.

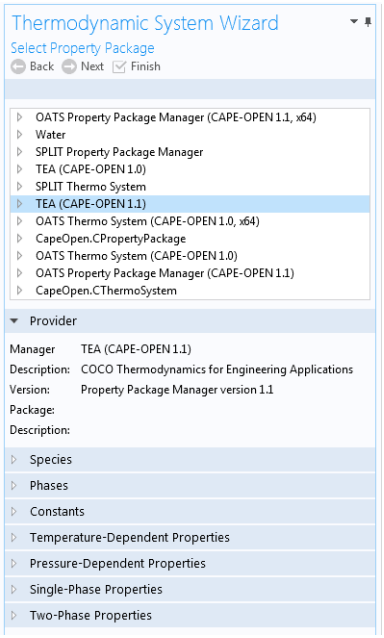


Figure 6-9: Available external thermodynamic systems. Use the Thermodynamic System Wizard to browse the contents of the installed external thermodynamic systems on your system. The example shows the packages shipped with the COCO provider.

SETTINGS

Selecting the **External Thermodynamic System** node shows the thermodynamic system settings with sections for available species, phases, species properties, and mixture properties. Editing the text in the Label text field changes the name of the system. Below follows a description of the thermodynamic system settings.

Provider

Contains information about the external thermodynamic system provider such as version, CAPE-OPEN compliance, and a short description of the external software that provides the thermodynamic system.

Species

Lists the species included in the selected thermodynamic system.

Phases

Lists the phases included in the selected thermodynamic system for example gas, liquid, gas-vapor, or liquid-liquid.

Species Properties

Lists the parameter values or the functions that describe species properties, for example molar mass, and properties available for pure compounds, such as density as a function of temperature.

Mixture Properties

Lists the available functions that describe mixture properties. One example is the density of a nonideal mixture as a function of composition.

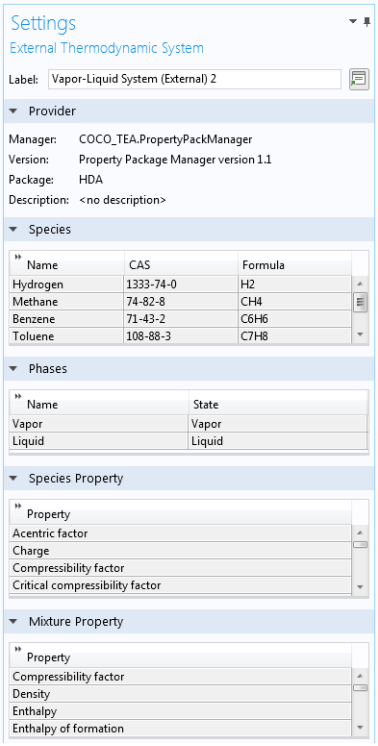


Figure 6-10: Settings window for an External Thermodynamic System.

The thermodynamic functionality supports package *persistence*. This means that an mph-file for a model that uses a thermodynamic system stores that package definition in the file. You can use the mph-file to access a thermodynamic system defined in the corresponding model without having to store the thermodynamic system as a separate file.

Predefined System

A **Predefined System** uses the built-in database with native functionality to set up one of the following common systems; dry air, moist air, or water and steam.

To create a **Predefined System**, start the **Thermodynamic System Wizard** in one of the following ways:

- Right-click the **Global Definitions** node, select **Thermodynamics** and choose **Predefined System**.
- Using the Reaction Engineering interface, choose **Predefined System** from the **Thermodynamics** section of the **Reaction Engineering** toolbar.
- Correspondingly, using the Chemistry interface, choose **Predefined System** from the **Thermodynamics** section of the **Chemistry** toolbar.

The **Thermodynamic System Wizard** that opens is identical to the wizard used to create a Thermodynamic System, but with the important difference that all settings have been entered for the chosen predefined system. The wizard contains the following steps:

1 Select System

2 Select Species

3 Select Thermodynamic Model

SELECT SYSTEM

In the Select System window, choose one of the predefined systems in the list. Choose among **Dry air**, **Moist air** and **Water-steam**. Click the Next button ( ) to proceed to the next step in the wizard.

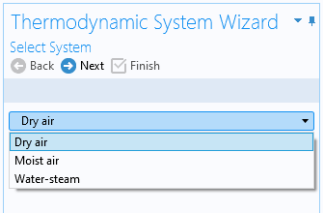


Figure 6-11: Thermodynamic System Wizard: Select Predefined System.

SELECT SPECIES

If Dry or Moist air was chosen in the Select System step, the **Selected species** table is populated with the species relevant for the chosen system. For Dry air the species are: nitrogen, oxygen, argon, carbon dioxide, neon and helium. For Moist air the list also contains water. If instead Water-steam was chosen in the Select System step, the Next button in that step guides you directly to the Select Thermodynamic Model pane. No additions of species can be done in the wizard.

To add more species to the Dry air and Moist air systems, use the **Species** Type filter text field to search among the available species in the **COMSOL** database or the User-Defined Species. Species can be searched for by typing the name, CAS number, or the chemical formula. Select one or more species in the list and click the **Add Selected** button ( ) to add species to the **Selected species** table. To remove species from the Selected species table, use either the Remove Selected button ( ) or the Remove All button ( ), both located below the table. Click the **Next** button ( ) to proceed to the next step in the wizard.

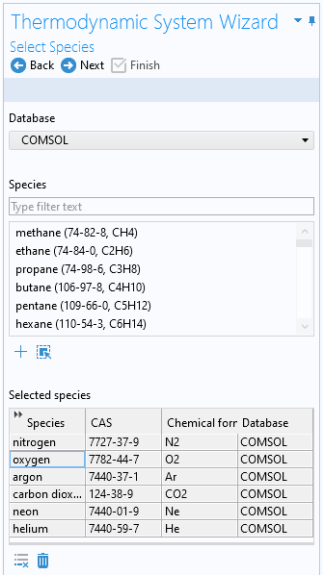


Figure 6-12: Thermodynamic System Wizard: Select Species.

SELECT THERMODYNAMIC MODEL

This last step of the Thermodynamic System Wizard allows you to choose what thermodynamic model to use. For the system Dry air and Moist air, the Ideal Gas law is chosen by default. For Water-steam, the model Water (IAPWS) is used. For more information about this step in the Thermodynamic System Wizard, see Select Thermodynamic Model for Thermodynamic System.

Click the **Finish** button ( ) to exit the **Thermodynamic System Wizard** and add the corresponding **Predefined System** under the **Thermodynamics** node. Note that the default node label reflects the chosen predefined system.

SETTINGS

Selecting a **Predefined System** node shows its **Settings** window with a description of the package content and the available properties. For information about the content in the Settings window, see Settings for **Thermodynamic System** and **Predefined System**.

MODIFYING A PREDEFINED SYSTEM

Please see Modifying an Existing System for information about how to modify an existing thermodynamic system.

Exporting and Importing Thermodynamic Systems

EXPORT THERMODYNAMIC SYSTEM

Right-click the thermodynamic system node for the thermodynamic system that you want to export (Figure 6-8) and select **Export Thermodynamic System**. Use the **Select File** window to store the thermodynamic system.

Note that only the thermodynamic system definition is exported, for example the underlying species data (from the database), the included phases, and the applied thermodynamic models. Property values and functions created using the thermodynamic system are not stored.

IMPORT THERMODYNAMIC SYSTEM

Right-click the **Thermodynamics** node and select **Import Thermodynamic System** (Figure 6-2). Use the **Select File** window to navigate to a thermodynamic system file and click **Open**.

Species Property

A **Species Property** is used to define and compute a pure species property. The available properties consist of both parameters and functions. Some examples of available parameters are molar mass, Lennard Jones diameter, and dipole moment. Some examples of available functions are density, enthalpy, heat capacity, and viscosity. The property functions created are either dependent on temperature alone, or both on temperature and pressure. For all property functions, the first order derivative with respect to temperature and, when applicable, with respect to pressure are automatically defined.

Right-click the relevant **Thermodynamic System** node (see Figure 6-8), **Predefined System** node, or the relevant **External Thermodynamic System** node, and select **Species Property** ( ) to start the **Species Property Wizard**.

The **Species Property Wizard** contains the following steps:

1 Select Properties

2 Select Phase

3 Select Species

4 Species Property Overview

SELECT PROPERTIES

First use the **Amount base unit** list to define the base unit. Select **mol** or **kg**.

Use the filter to search among the available properties. Select one or more properties in the list and click the **Add Selected** button ( ) to add them to the **Selected properties** list.

Click the **Next** button ( ) to proceed to the next step, selecting the species.

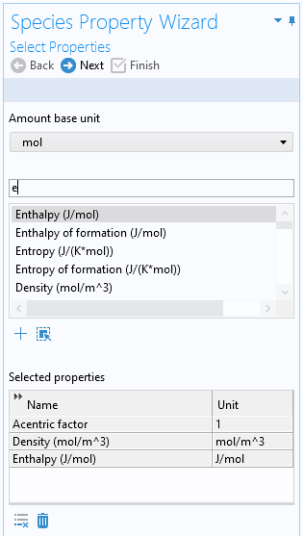


Figure 6-13: Species Property Wizard; Select Properties.

SELECT PHASE

Use the list to specify the phase for the species property. The available phases correspond to the ones defined for the thermodynamic system.

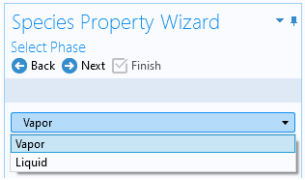


Figure 6-14: Species Property Wizard; Select Phase.

Note that for parameters (constants) this step is skipped.

SELECT SPECIES

Select one or more of the species available in the thermodynamic system and use the **Add Selected** button ( ) to add them to the **Selected species** table. One property function is created for each of the selected species.

Click the **Next** button ( ) to proceed to the next step in the wizard, which is selecting the phase for the property.

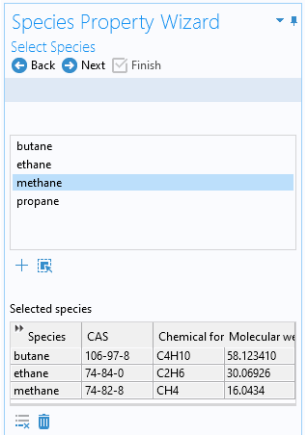


Figure 6-15: Species Property Wizard; the Select Species step.

SPECIES PROPERTY OVERVIEW

The final step of the wizard presents an overview of the parameters and functions defined for the corresponding property. Click the **Finish** button ( ) to exit the wizard and add the species property to the current thermodynamic system.

THE SPECIES NODE UNDER A SYSTEM

When creating a species properties, the resulting parameters and functions are collected under a node with the species name. You can create new functions from an existing species node under the system. Right-click the species and select **Species Property** to start the **Species Property Wizard**.

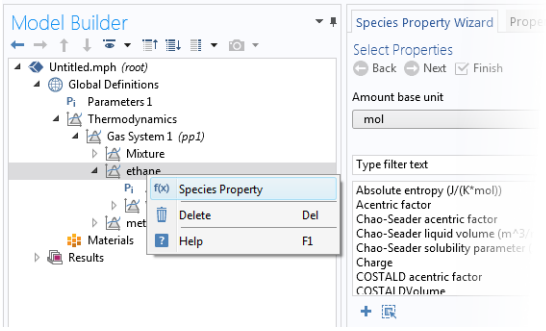


Figure 6-16: Create a Species Property from an existing species node.

SETTINGS

Selecting a **Species Property** node shows the settings for such property.

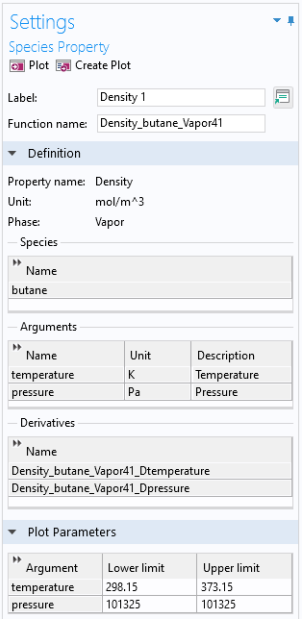


Figure 6-17: Species Property settings.

Definition:

Shows the definition of a property that is defined as a parameter or a function, for example the name of the parameter or function.

You can use the **Parameter name** or **Function name** fields to specify or change the name of a parameter or a function. The section also provides information about the property type and the species it is defined for.

For a parameter, this section also displays the numerical value.

For a function, this sections displays the arguments for the functions and the first order derivatives with respect to these arguments.

Plot Parameters

Available for property functions in order to plot a selected function for a given set of argument values.

Apply a **Lower limit** and an **Upper limit** for each argument, and click the **Plot** button ( ) to plot the function using the given argument range. You can also click the **Create Plot** button ( ) in order to create a plot group, under the **Results** node.

Properties Window

To see the reference for constant or temperature dependent functions, right-click on the function and select **Properties**. This opens the Properties window.

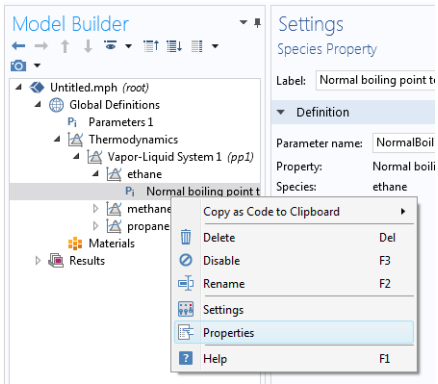


Figure 6-18: Show constant and temperature dependent properties references for species functions.

The reference for the constant or temperature dependent property is available in the **Comments** field in the **Node Properties** section.

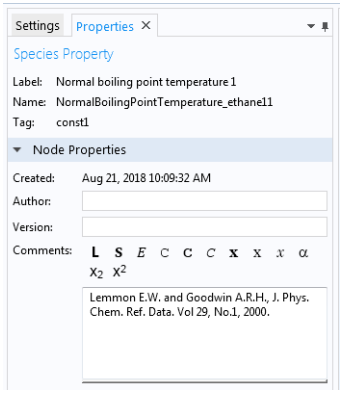


Figure 6-19: Properties window for species function.

Mixture Property

A **Mixture Property** is used to compute a property function that depends on the concentration of the species in a thermodynamic system. Some examples of the available property functions are density, enthalpy, heat capacity, and surface tension.

Apart from the composition, the mixture property functions are also dependent on temperature and pressure. The first-order derivatives with respect to temperature and pressure are automatically defined.

Right-click the relevant **Thermodynamic System** node (see Figure 6-8), **Predefined System** node, or the relevant **External Thermodynamic System** node, and select **Mixture Property** to start the **Mixture Property Wizard**.

The **Mixture Property Wizard** contains the following steps:

1 Select Properties

2 Select Phase

3 Select Species

4 Mixture Property Overview

SELECT PROPERTIES

The settings in this step corresponds to those for Select Properties in the **Species Property Wizard**. Click the **Next** button ( ) to proceed to the next step.

SELECT PHASE

Use this list to specify the phase, among the ones available in the system, for the selected mixture property.

Some properties require that the system consists of two phases, for example surface tension. A two-phase system may consist of a combination of liquid-vapor or liquid-liquid phases.

SELECT SPECIES

First select the **Species composition** base unit to be used for function arguments. Select **Mole fraction** or **Mass fraction**.

Select the species to be included in the list. Use the **Add All** button ( ) to add all species in the thermodynamic system. It is also possible to select a subset of the available species. In that case use the **Add Selected** button ( ) to add species. The **Selected species** table is updated as you add species.

Click the **Next** button ( ) to proceed to the next step in the wizard.

MIXTURE PROPERTY OVERVIEW

The final step of the wizard displays an overview of the parameters and functions that the wizard has added. Click the **Finish** button ( ) to exit the wizard and add the properties to the current thermodynamic system.

SETTINGS

Selecting a desired **Mixture Property** node to display its settings window.

THE MIXTURE NODE UNDER A SYSTEM

When creating mixture properties, the resulting functions are collected under the **Mixture** node. You can create new functions from an existing **Mixture** node. Right-click the node and select **Mixture Property** from the context menu to start the **Mixture Property Wizard**.

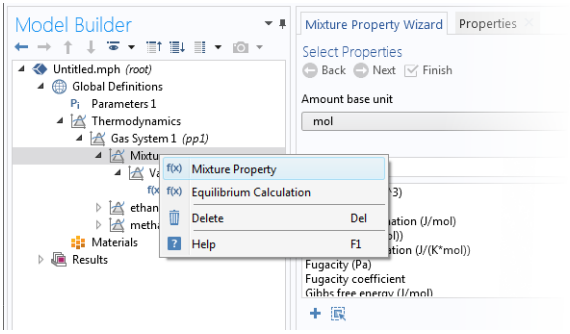


Figure 6-20: Mixture properties can be created by right-clicking a Mixture node under a thermodynamic system.

Equilibrium Calculation

The **Equilibrium Calculation** functionality is used to compute the resulting equilibrium conditions for a mixture of a set of species and phases.

Equilibrium calculations are often used for processes with vapor-liquid equilibrium (VLE), so-called flash calculations. A typical process that requires flash calculations is a distillation process, where a multiphase feed stream is separated into a vapor and a liquid product, and where the concentrations of the species in each phase are required. Equilibrium calculations involve combining the VLE-equations with material balances

for the chemical species, and in some cases with an energy balance. Flash calculations are typically used to obtain estimates of:

- Bubble point at given temperature.
- Bubble point at given pressure.
- Dew point at given temperature.
- Dew point at given pressure.
- Equilibrium conditions at given pressure and temperature.
- Equilibrium conditions at given pressure and enthalpy.
- Equilibrium conditions at given pressure and entropy.
- Equilibrium conditions at given internal energy and specific volume.

The last three examples are often considered more difficult, since they require energy balances and relations for computing enthalpy and entropy. The Liquid & Gas Properties Module can handle all of the above cases using the equilibrium calculation functionality. Phase envelopes, bubble point, and dew point can be calculated for any number of species.

Right-click the relevant **Thermodynamic System** node (see Figure 6-8), **Predefined System** node, or the relevant **External Thermodynamic System** node, and select **Equilibrium Calculation** to start the **Equilibrium Calculation Wizard**.

The **Equilibrium Calculation Wizard** consists of the following steps:

1 Select species
2 Equilibrium Specifications
3 Equilibrium Function Overview

The **Equilibrium Calculation** settings include three types of equilibrium functions.

- The first function type is used to detect whether a phase is present in the system and includes "exist" in its name.
- The amount function computes the total amount of material in each phase.
- The phase composition functions compute the mass or mole fraction of each species in each phase, depending on the selected base unit for the equilibrium calculation.

SELECT SPECIES

Select one or more of the species available in the thermodynamic system and use the **Add Selected** button ( ) to add them to the **Selected species** table. Click the **Next** button ( ) to proceed to the next step in the wizard.

EQUILIBRIUM SPECIFICATIONS

Use the **Amount base unit** list to use either **kg** or **mol** as base unit.

Select two **Equilibrium conditions** that define the current equilibrium, for example a given pressure and a temperature. These equilibrium conditions are used as arguments in the equilibrium functions, in addition to the composition (overall fractions of species).

The available equilibrium conditions are: **Temperature**, **Pressure**, **Phase fraction**, **Energy** (or **Internal energy of formation)**, **Enthalpy** (or **Enthalpy of formation)**, **Specific volume**, **Density** and **Entropy** (or **Entropy of formation**). For chemical reactions, it is recommended to use **Enthalpy of formation**, **Entropy of formation,** or **Internal energy of formation**, since they account for heat of reactions.

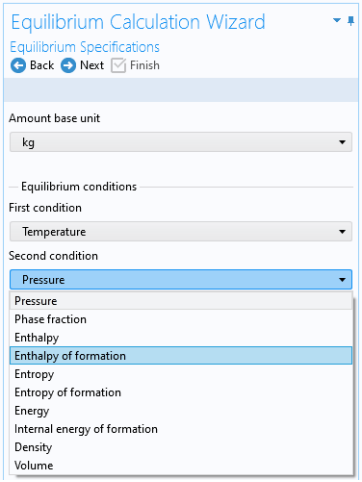


Figure 6-21: Equilibrium Calculation Wizard; Equilibrium Specifications.

Selecting **Phase fraction** as one of the equilibrium conditions activates the **Solution type** input field. This can be used to indicate the direction of the desired solution, which is of great use especially near critical points. The options **Undefined**, **Normal**, or **Retrograde** define different directions for the search of the solution to the equilibrium equations. Using **Normal** means that the derivative of the vapor phase fraction with respect to temperature (at constant pressure and composition) is kept positive and the derivative of the vapor phase fraction with respect to pressure (at constant temperature and composition) is kept negative. Using **Retrograde** means that the opposite sign of the previous mentioned derivatives are enforced.

For a single species, the critical point is the highest pressure and temperature at which two phases (liquid and vapor) are distinguishable. However, for some multispecies systems, the critical point is a point between the dew point and the bubble point. In this case, the critical point does not represent the maximum pressure or the maximum temperature of vapor-liquid coexistence. This phenomena is known as retrograde condensation. This means that under isothermal conditions, when the pressure decreases, some of the vapor condenses into liquid instead of expanding or vaporizing. An example of such system is formation of liquid hydrocarbons in a gas reservoir as the pressure decreases below the dew point pressure. In this case, setting **Solution type** to **Normal** or **Retrograde** may not be sufficient to distinguish between the two solutions.

Note that the **Solution type** setting is only available for a built-in thermodynamic systems. For external thermodynamic systems, the corresponding functionality needs to be supplied by the thermodynamic software provider. For instance, the COCO/TEA provider does not support the **Normal** or **Retrograde** options. In those cases, the **Solution type** should be **Undefined**.

Click the **Next** button ( ) to proceed to the next step.

EQUILIBRIUM FUNCTION OVERVIEW

In this step, you can review all the functions including units and arguments. Click the **Finish** button ( ) to exit the wizard and add functions at equilibrium state to the current thermodynamic system.

THE EQUILIBRIUM CALCULATION NODE

When creating an **Equilibrium Calculation**, the resulting functions are collected under the **Mixture** node. You can create new functions from an existing **Mixture** node. Right-click it and select **Equilibrium Calculation** to start the **Equilibrium Calculation Wizard** (see Figure 6-20).

SETTINGS

Selecting an **Equilibrium Calculation** node displays the settings including the property functions, see Figure 6-22.

Plot Parameters:

Can be used to evaluate and plot the equilibrium function for a range of argument values. First specify which of the included functions to plot. Then apply a **Lower limit** and **Upper limit** for each argument and click the **Plot** button ( ).

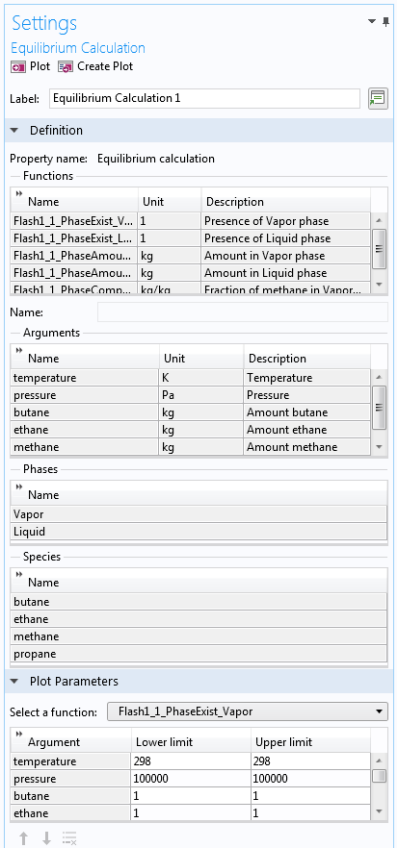


Figure 6-22: Settings window; Equilibrium calculation.

Generate Chemistry

The Chemistry physics interface includes functionality to automatically define and use mixture properties by interfacing to a Thermodynamic System node. How to manually set this coupling up is described in Coupling with the Reaction Engineering and the Chemistry Interfaces.

The **Generate Chemistry Wizard** can be used to directly create a Chemistry physics interface from an existing Thermodynamics System node. The resulting Chemistry interface is automatically populated with the selected species, and is set up to be fully coupled to the thermodynamics. This means for example that functions for mixture properties, like the density enthalpy, are automatically defined and used in the generated Chemistry interface.

Right-click the relevant **Thermodynamic System** node, **Predefined System** node, or **External Thermodynamic System** node, and select **Generate Chemistry** to start the **Generate Chemistry Wizard**.

The **Generate Chemistry Wizard** contains the following steps:

1 Select Species

2 Chemistry Settings

SELECT SPECIES

Select the species to be included in the list. Use the **Add All** button ( ) to add all species in the thermodynamic system. It is also possible to select a subset of the available species. In that case use the **Add Selected** button ( ) to add species. The **Selected species** table is updated as you add species.

Click the **Next** button ( ) to proceed to the next step in the wizard.

CHEMISTRY SETTINGS

The table at the top shows the selected species and their respective chemical formula. For each species, a corresponding Species feature will be added in the Chemistry interface. As an option, use the **Name in Chemistry** columns to specify another name of the species. By default the chemical formula is used.

Component

Use the **Component** list to select the model component to which the Chemistry interface will be added. The already existing components are shown in the top of the list. A new component can be created by selecting the desired space dimension.

Mass Transfer

The **Mass transfer** list controls the intended mixture type for the Chemistry interface. Select **Diluted species** to model a mixture where the species are assumed diluted in a high concentration solvent. For this choice, also select **Solvent**. Optionally, select **Concentrated species** to model a mixture where all species are assumed to contribute to

the mixture properties. In the resulting Chemistry interface the **Type** setting in the Mixture Properties section is defined accordingly.

Phase

Select the Phase of the mixture from the **Phase** list. Included in the list are the phases available in the Thermodynamic System from which the Chemistry is generated.

Click the **Finish** button ( ) to create the desired Chemistry physics interface and exit the wizard.

Generate Material

Once a thermodynamic system is defined, it can be used to define a multitude of property functions. The Generate Material option provides a fast route to defining the material properties most commonly required for fluid flow, heat transfer and mass transfer. By specifying the composition and the phase of the mixture, a Material node can automatically be setup. The material node can include properties such as the density, heat capacity, heat capacity ratio, thermal conductivity and the viscosity. Two types of property functions can be used. Either functions from the underlying thermodynamics can be used, or interpolation functions created from these. For space-dependent models, the interpolation models are more computationally efficient.

Right-click the relevant **Thermodynamic System** node (or an **External Thermodynamic System** node or **Predefined System** node), and select **Generate Material** to start the **Generate Material Wizard**.

The **Generate Material Wizard** contains the following steps:

1. Select Phase
2. Select Species
3. Select Properties
4. Define Material

SELECT PHASE

Use this list to specify the phase of the material. Select among the ones available in the system. This step of the Generate Material Wizard is not available for the **Predefined Systems Dry Air** and **Moist Air**.

Click the **Next** button ( ) to proceed to the next step in the wizard.

SELECT SPECIES

Select the species to be included in the list. Use the **Add All** button ( ) to add all species in the thermodynamic system. It is also possible to select a subset of the available species. In that case use the **Add Selected** button ( ) to add species. The **Selected species** table is updated as you add species.

Notice that when using Generate Material for the **Predefined System Water-steam** this step is not included in the wizard.

Material Composition

Specify the mixture composition in terms of the **Mole fractions** or **Mass fractions** of all species. The fractions should sum to one. This setting is only available for systems with more than one component, and for materials with more than one selected species.

Click the **Next** button ( ) to proceed to the next step in the wizard.

SELECT PROPERTIES

Use this step to select the material properties to be included.

For a liquid phase material the following properties are available:

- Density, (ρ)
- Diffusion coefficient at infinite dilution
- Heat capacity (C_p)
- Thermal conductivity (k)
- Viscosity (μ)

For a gas phase material, the Heat capacity ratio ($\gamma = C_p/C_v$) is also available.

To add a property to the **Selected properties** list click the **Add Selected** button ( ). To remove properties, use the **Remove Selected** button ( ) or the **Remove All** button ( )

When adding the **Diffusion coefficient at infinite dilution**, also select which of the species is the solvent. The material will include one diffusion coefficient for each of the remaining (solute) species.

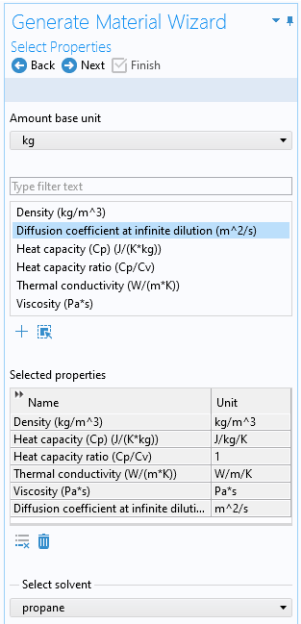


Figure 6-23: Generate Material Wizard; Select Properties with Diffusion coefficient at infinite dilution added.

Additional properties

The below additional properties are defined from the selected properties and added to the output properties of the material.

For a liquid phase material the isobaric coefficient of thermal expansion is defined as:

$$\alpha_{\text{iso}} = -\frac{1}{\rho}\frac{\partial \rho}{\partial T} \tag{6-1}$$

For a gas phase material, the speed of sound c, and the isentropic compressibility χ_f are also defined as:

$$c = \sqrt{\gamma \frac{\partial p}{\partial \rho}}, \qquad \chi_f = \frac{1}{\gamma \rho}\frac{\partial \rho}{\partial p} \tag{6-2}$$

Click the **Next** button ( ) to proceed to the next step.

Component

Use the **Component** list to select where the Material will be added. The already existing components are shown in the top of the list. A new component can be created by selecting the desired space dimension. Select **Global** at the end of the list to add the material under **Global Definitions**. A global material can be utilized in any component, through the use of a Material Link. It can also be used to define phase specific properties when linked to from a subnode of a **Porous Material**.

Function Type

The material can be set up to use functions defined under the thermodynamics system, or interpolation functions defined from these. The interpolation functions are significantly faster to evaluate, especially for space dependent models, but requires that the temperature range and the pressure range is specified.

Select **Thermodynamics** to base the material properties on functions in the current thermodynamic system. The required functions are created, if not already present, and added to the system. When evaluating material properties, the underlying thermodynamics functions are called.

Select **Interpolation** to generate interpolation functions for the material properties. In this case the required functions are first created and added to the system. Next, the functions are evaluated in a number of sampling points over a given range, for both temperature and pressure. The result of the evaluation is stored and used to define interpolation functions for all material properties.

For the **Interpolation points**, select **Same for all functions** to use the same number of evaluation points for all function. By selecting **Individual**, the number of evaluation points can be given per function. The latter can for example be used to increase the number of points for a function that is known to vary faster than the rest of the functions.

Select one of the preset levels for the **Maximum number of interpolation points**. This is used to provide a maximum size of the underlying data for the interpolation functions. If the total number of evaluation points for any function, varying temperature and pressure, is exceeded, a warning is shown.

Define the temperature range for the temperature and pressure by providing the **Low** and **High** end values. To neglect the variation in either temperature or pressure, give the same value for the low and high end value. This can for example be used when the pressure variation is known to be negligible. For each range, also define the number of

evaluation points in the **Number of points** field. The underlying functions are evaluated at uniformly distributed positions across the temperature and pressure range.

When **Individual** has been selected for the **Interpolation points**, the **Ranges and interpolation points** can be specified per function to be created.

Click the **Finish** button (☑) to create the specified Material and exit the wizard.

Coupling with the Reaction Engineering and the Chemistry Interfaces

Using the **Reaction Engineering** or **Chemistry** interfaces, all species property parameters and property functions required by these interfaces can be created automatically by coupling to an existing **Thermodynamic System**, **Predefined System**, or **External Thermodynamic System** under **Thermodynamics**. Examples of species properties that can be created automatically are molar mass, heat capacity, enthalpy, and entropy for each species. Parameters and functions for these properties are created by the thermodynamic system. The **Reaction Engineering** and **Chemistry** interfaces can also be used to define transport properties for the resulting mixture (all species in the interface). When coupled, the following mixture properties can be automatically created: heat capacity, density, thermal conductivity, and dynamic viscosity.

This Reaction Engineering interface and the Chemistry interface are only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

Note that using a thermodynamic system significantly increases the modeling capabilities in the **Reaction Engineering** and **Chemistry** interfaces. All ideal and nonideal thermodynamic models, for gases and liquids, are directly available and also automatically updated by editing the settings for the thermodynamic system in use. The **Chemistry** interface can furthermore be used to make the mixture properties readily available in space-dependent models for modeling of mass transport, heat transfer, or fluid flow.

REACTION ENGINEERING

Mixture Properties

You can couple a Reaction Engineering interface with an existing thermodynamic system in the **Reaction Engineering** interface's settings window.

You need to have at least one species defined in the Reaction Engineering interface in order to couple it to a thermodynamic system. You can make this coupling in the Settings window for the **Reaction Engineering** interface by selecting the **Thermodynamics** check box in the **Mixture Properties** section.

Select a thermodynamic system from the **Thermodynamic system** list. Use the **Phase** list to select the phase to be used in the **Reaction Engineering** interface.

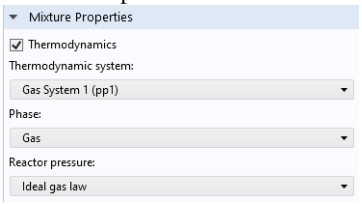


Figure 6-24: Coupling Reaction Engineering Interface with Thermodynamics.

Species Matching

The **Species Matching** section is activated when the **Thermodynamics** check box is selected in the **Mixture Properties** section; see above. The species in the Reaction Engineering interface can be matched to a species in the thermodynamic system. This step ensures that the arguments in the thermodynamic system functions are correctly defined.

Use the lists in the **From Thermodynamics** column to match each species in the interface to a species in the coupled thermodynamic system.

For each species matched, the required property parameters and functions are added under to the corresponding thermodynamic system.

When all species are matched, the interface is considered fully coupled and functions representing mixture properties, such as density, are also added automatically under the corresponding thermodynamic system.

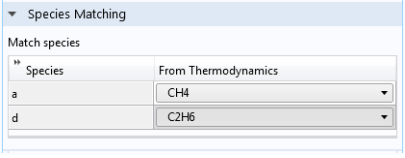


Figure 6-25: Matching the species in Reaction Engineering to those in the corresponding thermodynamic system.

Calculate Transport Properties

When the interface is fully coupled to a thermodynamic system, property functions for the mixture transport properties are created automatically when the **Calculate mixture properties** check box is selected. The properties calculated by the thermodynamic system display **Thermodynamics** in the corresponding list; see below.

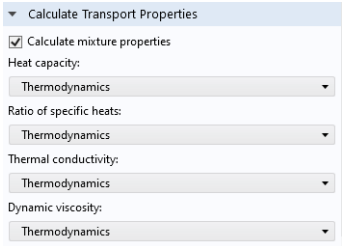


Figure 6-26: Select the Calculate mixture properties check box when coupled to a thermodynamic system.

CHEMISTRY

Mixture Properties

You can couple a Chemistry interface with an existing thermodynamic system in the **Chemistry** interface's settings window. You can make this coupling in the Settings window for the **Chemistry** interface by selecting the **Thermodynamics** check box in the **Mixture Properties** section. You need to have at least one species defined in the Chemistry interface in order to couple it to a thermodynamic system.

Select a thermodynamic system from the **Thermodynamic system** list. Use the **Phase** list to select the phase to be used in the **Chemistry** interface.

Species Matching

The **Species Matching** section is activated when the **Thermodynamics** check box is selected in the **Mixture Properties** section. Here you can match the variables for the concentrations, and by this calculate mixture properties (transport and thermodynamic properties). For information on how to specify the dependent variables to be used, see Species Matching in The Chemistry Interface documentation.

You can match the species in the Chemistry interface with those in the corresponding thermodynamic system in the **Species matching** section's table. Use the lists in the column with the title **From Thermodynamics** to match each species in the Chemistry interface to a species in the corresponding thermodynamic system. This ensures that the composition function arguments in the thermodynamic system are correctly defined.

For each species matched, the species property parameters and functions required by the Chemistry interface are automatically created and added under the corresponding thermodynamic system.

When all species are matched, the interface is fully coupled to Thermodynamics and functions representing mixture properties, such as the density, are added automatically under the thermodynamic system that the interface is coupled to.

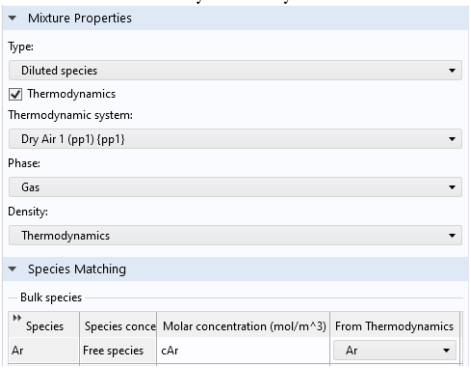


Figure 6-27: Matching concentration variables in a Chemistry interface, as well as species in a coupled Thermodynamic System.

Calculate Transport Properties

When the interface is fully coupled to a thermodynamic system, property functions for the mixture transport properties are created automatically when the **Calculate mixture properties** check box is selected. The properties calculated by the thermodynamic system display **Thermodynamics** in the corresponding list; see Figure 6-26.

MIXTURE PROPERTY DEFINITIONS WHEN COUPLING TO THERMODYNAMICS

When all species in a physics interface are matched to the corresponding species in a thermodynamic system, the mixture properties are calculated based on the composition of the mixture. For example, consider $Z_{\text{mix}}(T, P, n_1, \ldots, n_m)$, which denotes a generic extensive mixture property for a mixture of m number of species. The property function's arguments are temperature T, pressure P, and the number of moles, n, for each species.

When the system is fully matched, the mixture property Z_{mix} is defined as:

$$Z_{\text{mix}} = \sum_{i=1}^{m} n_i \bar{Z}_i \tag{6-3}$$

where $\bar{Z}_i$ is the partial molar of species i:

$$\bar{Z}_i = \left(\frac{\partial Z_{\text{mix}}(T, P, n_1, n_2, \ldots, n_m)}{\partial n_i}\right)_{T, P, n_{j \neq i}} \tag{6-4}$$

The definition of partial molar properties can be rewritten using mole fraction derivatives as:

$$\bar{Z}_i(T, P, n_1, \ldots, n_m) = \bar{Z}_i(T, P, x_1, \ldots, x_m) = \tag{6-5}$$

$$\left(Z_{\text{mix}}(T, P, x_1, \ldots, x_m) + \left(\frac{\partial Z_{\text{mix}}(T, P, x_1, \ldots, x_m)}{\partial x_i}\right)_{T, P, x_{i \neq j}} - \sum_{i=1}^{m}\left(x_i\left(\frac{\partial Z_{\text{mix}}(T, P, x_1, \ldots, x_m)}{\partial x_i}\right)_{T, P, x_{i \neq j}}\right)\right)$$

When the system is partially coupled, which means that some but not all species have been coupled, the mixture property is instead calculated assuming ideal mixing:

$$Z_{\text{mix}} = \sum_{i=1}^{m} n_i Z_i(T, P) \tag{6-6}$$

using the pure species properties $Z_i = Z_{\text{mix}}(T, P, x_i = 1, 0, \ldots, 0)$.

Evaluating a Property Function in a Physics Interface

The functions set up using a thermodynamic system in Thermodynamics can be used directly in any physics interfaces in COMSOL Multiphysics, in the same way as for standard functions. Simply type in the function name with the proper arguments in the appropriate field of the model to use the function. Figure 6-28 shows an example of this from the Reaction Engineering interface. In this example, the **Species Thermodynamic Expressions** section gets input for the molar entropy, the enthalpy and the heat capacity of toluene. These functions, generated using **Species Property** for a

thermodynamic system containing toluene, have been entered in the corresponding input fields using the appropriate arguments.

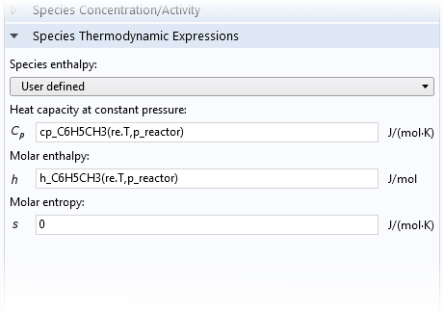


Figure 6-28: The enthalpy and heat capacity of toluene are evaluated using property calculations through a thermodynamics system. In this case, the functions are temperature and pressure dependent properties for a pure component.

User-Defined Species

Use this feature to specify the properties of a new species not available in the included COMSOL database. This feature can also be used to edit a database species, by using an existing species as a template, to create a new one. A User-Defined Species can be included in a Thermodynamic System feature, or Predefined System feature, together with predefined database species and other user-defined species.

The data needed for a user-defined species includes both material properties, such as the molar mass and the vapor pressure, and properties for specific thermodynamic models or transport models (see Thermodynamic Models and Theory). For instance, in order to use the UNIFAC thermodynamic model, you need to define UNIFAC groups for the new species.

Note that the thermodynamics calculator includes measures to handle missing species properties, sometimes by applying approximations. For instance, if the Wilson volume is not available, the liquid volume at normal boiling point is used instead. If data for this is also missing, it is estimated from the saturated liquid density correlation.

When creating a user-defined species it is recommended to add the following common material properties:

- Molecular mass
- Critical properties
- Acentric factor

- Absolute entropy
- Standard enthalpy of formation
- Ideal gas heat capacity
- Vapor pressure
- Heat of vaporization
- Saturated liquid density
- Transport properties

EXAMPLE MODEL

For an example of using a User-Defined Species see this application example:

Dissociation in a Tubular Reactor: Application Library path **Chemical_Reaction_Engineering_Module/Thermodynamics/dissociation**

THE USER-DEFINED SPECIES WIZARD

To create a **User-Defined Species**, start the **User-Defined Species Wizard** in one of the following ways:

- Right-click the **Global Definitions** node, select **Thermodynamics** and choose **User-Defined Species**.
- If the model already includes the **Thermodynamics** node, right-click it and choose **User-Defined Species**.
- Using the Reaction Engineering interface, or **Chemistry** interface, choose **User-Defined Species** from the **Thermodynamics** section of the **Reaction Engineering**, or **Chemistry** toolbar.

The **User-Defined Species Wizard** contains the following steps:

1 Enter Name and Formula

2 Enter Parameters

3 Define Properties

ENTER NAME AND FORMULA

Enter the **Name**, **CAS** number, and the **Chemical formula** for the new species.

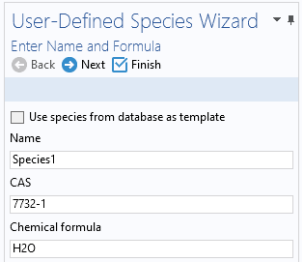


Figure 6-29: User-Defined Species Wizard; Enter Name and Formula.

If you want to edit a species in the COMSOL database, select the **Use species from database as template** check box. Then locate the species to edit in the list. The filter text field can be used to search among the available species.

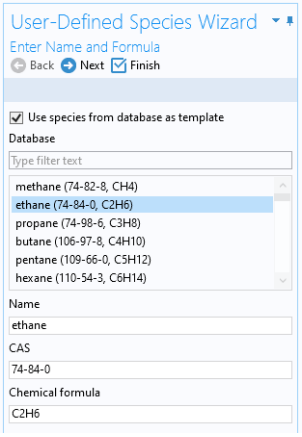


Figure 6-30: User-Defined Species Wizard; edit an available species by selecting Use species from database as template.

Click the **Next** button ( ) to proceed to the next step.

ENTER PARAMETERS

Define the necessary parameter for the new species.

Constants

Use this table to define material constants such as molar mass, critical temperature, and standard enthalpy of formation.

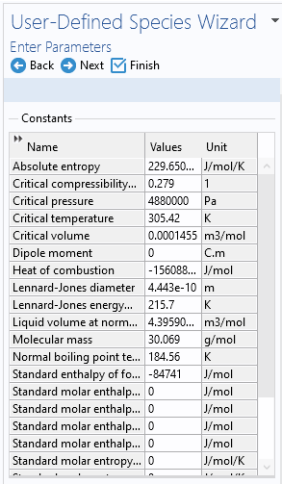


Figure 6-31: User-Defined Species Wizard; Enter material constants.

Structure information

If you want to use the UNIFAC model, specify the structure formula, the UNIFAC groups and their number occurrences.

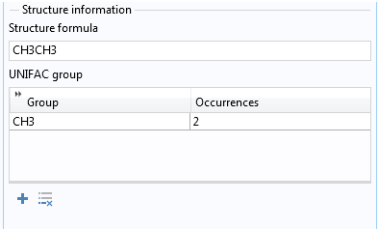
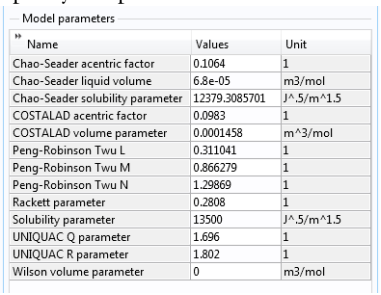


Figure 6-32: User-Defined Species Wizard; Specify the structure information in the Enter Parameters step.

Model parameters

Specify the parameters for the thermodynamic models and transport models in use.


Model parameters

Name	Values	Unit
Chao-Seader acentric factor	0.1064	1
Chao-Seader liquid volume	6.8e-05	m3/mol
Chao-Seader solubility parameter	12379.3085701	J^.5/m^1.5
COSTALAD acentric factor	0.0983	1
COSTALAD volume parameter	0.0001458	m^3/mol
Peng-Robinson Twu L	0.311041	1
Peng-Robinson Twu M	0.866279	1
Peng-Robinson Twu N	1.29869	1
Rackett parameter	0.2808	1
Solubility parameter	13500	J^.5/m^1.5
UNIQUAC Q parameter	1.696	1
UNIQUAC R parameter	1.802	1
Wilson volume parameter	0	m3/mol

Figure 6-33: User-Defined Species Wizard; Specify model parameters.

Click the **Next** button ( ) to proceed to the next step.

DEFINE PROPERTIES

The last step in the wizard is to add temperature dependent properties for the new species. All temperature dependent properties are defined using cubic polynomials on the form

$$f(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3 \qquad (6\text{-}7)$$

Each property can consist of an arbitrary number of temperature intervals, each using the above form. Click the **Add** button ( ) under the table for a specific property to add an interval.

The following temperature dependent properties are necessary in order to compute the basic set of mixture properties when including the **User-Defined Species** in a thermodynamic system:

- Ideal gas heat capacity
- Liquid density
- Vapor pressure
- Heat of vaporization

Note that some thermodynamic properties, such as the enthalpy and entropy, of a species or mixture, are estimated from the ideal gas heat capacity and depends on the thermodynamic model applied for the system (see Thermodynamic Properties Definitions).

Click the **Finish** button ( ) in the top of the Settings window to finalize the species and add it to the **User-Defined Species** node under **Thermodynamics**.

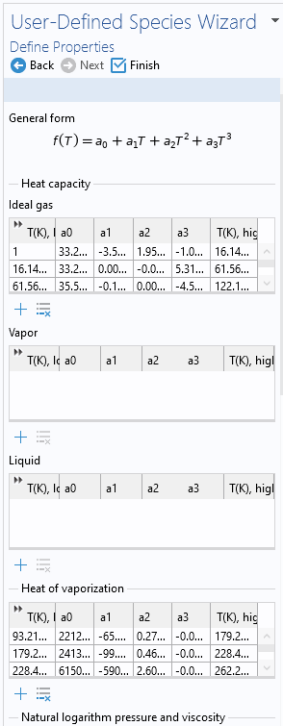


Figure 6-34: User-Defined Species Wizard; specify temperature-dependent properties.

SETTINGS

Selecting a species node under **User-Defined Species** shows the Settings window including the definitions of all species properties. Properties are categorized into sections as seen in Figure 6-35 below. All properties can be edited by expanding the corresponding section.

	When a species properties has been changed, any **Thermodynamic System** that includes the species needs to be updated for the changes to take effect (see Update From Species).

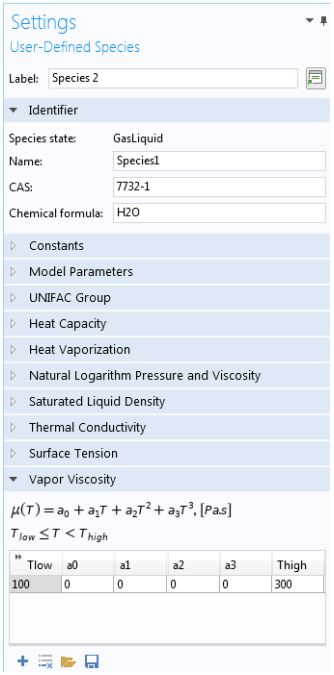


Figure 6-35: The Settings window for a User-Defined Species.

References

1. www.colan.org

2. Cape Open to Cape Open Simulation Environment, www.cocosimulator.org/index_download.html

Thermodynamic Models and Theory

In this section:

- Introduction
- Thermodynamic Models
- Selecting the Right Thermodynamic Model
- Species Property References
- Thermodynamic Properties Definitions
- Standard Enthalpy of Formation and Absolute Entropy Terms
- Reference State
- Transport Properties
- Surface Tension
- References

Introduction

In this chapter, we review the theory behind the thermodynamic properties database and its functions. The thermodynamic models in the database are available for single phase, gas or liquid, and phase equilibrium systems for two or more phases such as vapor-liquid equilibrium (VLE), vapor-liquid-liquid equilibrium (VLLE) and liquid-liquid equilibrium (LLE).

Thermodynamic Models

In the following sections, the available thermodynamic models are described:

- Equation of State Models
- Liquid Phase Models

EQUATION OF STATE MODELS

An equation of state (EOS) model is an algebraic relation between the absolute pressure (P), the molar volume (V), and the absolute temperature (T). An equation of state that is at least cubic in volume and in the form of

$$Z \equiv \frac{PV}{RT} = f_v(V, T) \tag{6-8}$$

where Z is the compressibility factor and R the universal gas constant, can be used to describe both gases and liquids. The cubic equations of state are widely used to describe the gaseous and liquid volumetric behavior of pure fluids and also all other properties with extensions to mixtures. A comprehensive comparisons of different cubic EOS can be found in Ref. 4 and Ref. 5.

The equation of state models available in the thermodynamic properties database are:

- Ideal Gas Law
- Peng-Robinson
- Peng-Robinson (Twu)
- Soave-Redlich-Kwong
- Soave-Redlich-Kwong (Graboski-Daubert)
- Water (IAPWS)

Ideal Gas Law

The ideal gas law equation of state is

$$P = \frac{RT}{V} \tag{6-9}$$

As the name suggests, the ideal gas law is only applicable to gases. In fact, its use is limited to gases at low to moderate pressures.

Peng-Robinson

The classical Peng-Robinson (PR) equation of state Ref. 7 is given by

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V^2 + 2bV - b^2} \tag{6-10}$$

where for species i,

$$a_i = \Omega_A \frac{R^2 T_c^2}{P_c} \tag{6-11}$$

$$b_i = \Omega_B \frac{RT_c}{P_c} \tag{6-12}$$

$$\Omega_A = \frac{1}{3} + \frac{1}{3}\Omega_B(4 + 10\Omega_B) \tag{6-13}$$

$$\Omega_B = \left(\beta - \frac{63}{1024\beta} - 0.03125\right) \tag{6-14}$$

The alpha function, α_i, is given by

$$\alpha_i = [1 + (0.37464 + 1.54226\omega_i - 0.26992\omega_i^2)(1 - \sqrt{T_{r,i}})]^2 \tag{6-15}$$

For mixtures

$$a\alpha = \sum_i \sum_j x_i x_j (1 - k_{\mathrm{PR,i,j}}) \sqrt{(a\alpha)_i (a\alpha)_j} \tag{6-16}$$

$$b = \sum_i x_i b_i \tag{6-17}$$

The binary interaction parameters (BIPs), k_{PR}, are symmetric with zeros in the diagonal:

$$k_{\mathrm{PR}} = k_{\mathrm{PR,i,j}} \tag{6-18}$$

$$k_{\mathrm{PR,i,j}} = 0 \tag{6-19}$$

When binary interaction parameters are missing in the database for a set of species, the value is set to zero (a warning node is created). The values for critical temperature, T_c, critical pressure, P_c, and acentric factor, ω_i must be specified for all species.

Peng-Robinson (Twu)

For the Twu modificationRef. 8 of the Peng-Robinson model, the alpha function, α_i, is replaced by

$$\alpha_i = T + R^{(N_i(M_i - 1))} \exp(L_i(1 - T_{r,i}^{N_i M_i})) \tag{6-20}$$

The binary interaction parameters k_{PR}, are used for the Twu modification. Acentric factor, ω_i, is not used in this model but critical temperature and critical pressure must be specified for all species. The species specific fit parameters L_i, M_i, N_i can be determined by fitting the pure species phase equilibrium to the vapor pressure curve.

Soave-Redlich-Kwong

The classical Soave-Redlich-Kwong equation of state Ref. 9 is given by

$$P = \frac{RT}{V - b} - \frac{a\alpha}{V(V + b)} \tag{6-21}$$

with

$$\alpha = \frac{1}{\sqrt{T}} \tag{6-22}$$

and for the pure species i,

$$a_i = \Omega_A \frac{R^2 T_c^{2.5}}{P_c} \tag{6-23}$$

$$b_i = \Omega_B \frac{RT_c}{P_c} \tag{6-24}$$

$$\Omega_A = \frac{1}{3} + \frac{1}{3}\Omega_B(3 + 3\Omega_B) \tag{6-25}$$

$$\Omega_B = \frac{1}{27} 2^{\frac{1}{3}} 27^{\frac{2}{3}} - \frac{1}{3} \tag{6-26}$$

For mixtures

$$a = \sum_i \sum_j x_i x_j (1 - k_{\mathrm{SRK,i,j}}) \sqrt{a_i a_j} \tag{6-27}$$

$$b = \sum_i x_i b_i \tag{6-28}$$

The binary interaction parameters, k_{SRK}, are symmetric with zero in the diagonal:

$$k_{SRK,\mathrm{i,j}} = k_{SRK,\mathrm{j,i}} \tag{6-29}$$

$$k_{SRK,\mathrm{i,j}} = 0 \tag{6-30}$$

If a value is missing for $k_{SRK,i,j}$ in the database, it is set to zero (a warning node is created). The Values for critical temperature, T_c, critical pressure, P_c, and acentric factor, ω_i, must be specified for all species. The Soave-Redlich-Kwong equation of state is a version of Equation 6-21 modified by Soave Ref. 10, where for pure species i, the alpha function is modified to

$$\alpha_i = [1 + (0.480 + 1.574\omega_i - 0.176\omega_i^2)(1 - \sqrt{T_{r,i}})]^2 \tag{6-31}$$

Soave-Redlich-Kwong (Graboski-Daubert)

The Graboski and Daubert Ref. 11 modification of the Soave-Redlich-Kwong equation of state replaces alpha function by

$$\alpha_i = [1 + (0.48508 + 1.55174\omega_i - 0.1561\omega_i^2)(1 - \sqrt{T_{r,i}})]^2 \quad (6\text{-}32)$$

except for H_2, where it is replaced by

$$\alpha_{H_2} = 1.202 \exp(-0.30228 T_{r,H_2}) \quad (6\text{-}33)$$

Water (IAPWS)

The International Association for the Properties of Water and Steam (IAPWS) provides a set of correlations to compute properties of water in different states. The correlations available in COMSOL correspond to the version named Industrial Formulation 1997 (IF-97) Ref. 12 - Ref. 14. The correlations are valid in the following ranges:

$$273.15\ \text{K} \le T \le 1073.15\ \text{K} \qquad p \le 100\ \text{MPa} \quad (6\text{-}34)$$

$$1073.15\ \text{K} \le T \le 2273.15\ \text{K} \qquad p \le 50\ \text{MPa} \quad (6\text{-}35)$$

The following water and steam properties, available by creating a Species Property, are computed using the IAPWS correlations: density, volume, enthalpy, internal energy, Helmholtz energy, heat capacity at constant pressure, and heat capacity at constant volume. The amounts present in the vapor and liquid phase can be computed using an Equilibrium Calculation.

Other parameters and thermodynamic properties available for the system are provided from COMSOL database.

LIQUID PHASE MODELS

Activity coefficient models

Activity coefficient models are used to describe liquid mixtures at low to moderate pressure and temperature but where equations of state are inadequate. When using activity coefficient models, the partial fugacity for species i in the liquid phase is defined as

$$\hat{f}_{i,l} = x_i \gamma_i \phi_{i,sat} P_{i,sat} F_i \quad (6\text{-}36)$$

which yields

$$\hat{\phi}_{i,\,l} = \gamma_i \phi_{i,\,sat} \frac{P_{i,\,\mathrm{sat}}}{P} F_i \tag{6-37}$$

where the activity coefficient, γ_i, describes the nonideal liquid phase and $\hat{\phi}_{i,\,sat} P_{i,\,sat}$ is the fugacity at the vapor-liquid phase boundary at equilibrium for the pure species i. The Poynting correction, F_i, describes the pure species fugacity deviation from the boiling curve and can be expressed as

$$F_i = \exp\left(\int_{P_{i,\,sat}}^{P} \frac{V_{i,\,l}}{RT} dp\right) \tag{6-38}$$

For an incompressible liquid, an approximation of the Poynting correction can be done according to

$$F_i \approx \exp\left(\frac{V_{i,\,l}}{RT}(P - P_{i,\,sat})\right) \tag{6-39}$$

The Poynting correction can often be ignored for moderate pressure. Hence, Equation 6-37 can be expressed as

$$\hat{\phi}_{i,\,l} = \gamma_i \phi_{i,\,sat} \frac{P_{i,\,sat}}{P} \tag{6-40}$$

If the vapor phase is considered ideal, then $\phi_{i,\,sat} = 1$ and the above equation reduces to

$$\hat{\phi}_{i,\,l} = \gamma_i \frac{P_{i,\,sat}}{P} \tag{6-41}$$

This reduction can be selected explicitly in case the vapor phase is not ideal.

The logarithmic transformation of Equation 6-37 is:

$$\ln \hat{\phi}_{i,\,l} = \ln \gamma_i + \ln \phi_{i,\,sat} + \ln P_{i,\,sat} - \ln P + \ln F_i \tag{6-42}$$

Ideal Solution

For an ideal solution the activity coefficient is equal to one, which gives:

$$\ln \gamma_i = 0 \tag{6-43}$$

Regular Solution

The Scatchard-Hilderbrand equation Ref. 16 for a nonpolar mixture is

$$\ln\gamma_i = \frac{V_i(\delta_i - \delta_{av})^2}{RT} \tag{6-44}$$

where V_i is species molar volume and δ_i is species solubility parameter, and δ_{av} is

$$\delta_{av} = \frac{\sum_i (x_i V_i \delta_i)}{\sum_i (x_i V_i)} \tag{6-45}$$

The volume parameter, V_i, is set equal the liquid volume, $V_{i,l,b}$ at normal boiling point which must be specified for all species. The solubility parameter, δ_i must be specified for all species and can be estimated from the normal heat of vaporization, $\Delta H_{vap,i}$ and the liquid volume at normal boiling point as below:

$$\delta_i \equiv \sqrt{\frac{\Delta H_{vap,i}}{V_{i,l,b}}} \tag{6-46}$$

Extended Regular Solution

The extended Scatchard-Hildebrand equation adds the Flory and Huggins correction to the regular solution model Ref. 18:

$$\ln\gamma_i = \frac{V_i(\delta_i - \delta_{av})^2}{RT} + \ln(\theta_i) + 1 - \theta_i \tag{6-47}$$

where

$$\theta_i = \frac{V_i}{\sum_i (x_i V_i)} \tag{6-48}$$

Wilson

Wilson Ref. 19 derived his activity coefficient model from a consideration of probabilities of neighboring molecules in a liquid

$$\ln\gamma_i = 1 - \sum_j \left(\frac{x_j \Lambda_{j,i}}{\sum_k x_k \Lambda_{j,k}} \right) - \ln\left(\sum_j x_j \Lambda_{i,j} \right) \tag{6-49}$$

$$\Lambda_{i,j} = \frac{V_{w,j}}{V_{w,i}} \exp\left(-\frac{\lambda_{i,j}}{T}\right) \tag{6-50}$$

where the Wilson volume parameter, $V_{w,i}$, is a species-specific parameter describing volume. If the volume parameter is not available, the liquid volume at normal boiling point is used. The Wilson binary interaction parameters $\lambda_{i,j}$ are specified in terms of absolute temperature. The binary interaction parameter matrix is nonsymmetric and with zeros in its diagonal. All off-diagonal values must be specified

$$\lambda_{i,i} = 0 \tag{6-51}$$

$$\Lambda_{i,i} = 1 \tag{6-52}$$

NRTL

Renon and Prausnitz (Ref. 20) formulated a three parameter activity coefficient model that is able to describe liquid-liquid equilibrium; the nonrandom two-liquid (NRTL) model:

$$\ln\gamma_i = \frac{\sum_j x_j \tau_{j,i} G_{j,i}}{\sum_j x_j G_{j,i}} + \sum_j \left(\frac{x_j G_{j,i}}{\sum_k x_k G_{k,j}} \left(\tau_{i,j} - \frac{\sum_k x_k \tau_{k,j} G_{k,j}}{\sum_k x_k G_{k,j}} \right) \right) \tag{6-53}$$

$$\tau_{i,j} = \frac{A_{i,j}}{T} \tag{6-54}$$

$$G_{i,j} = \exp(-\alpha_{i,j}\tau_{i,j}) \tag{6-55}$$

The three parameters are $A_{i,j}$, $A_{j,i}$, and $\alpha_{i,j}$. A more general form is implemented here:

$$\tau_{i,j} = \frac{A_{i,j}}{T} + B_{i,j} \tag{6-56}$$

$$G_{i,j} = \exp(\beta_{i,j} - \alpha_{i,j}\tau_{i,j}) \tag{6-57}$$

The binary interaction parameters, $A_{i,j}$, are specified in terms of absolute temperature. The diagonal values are zero and the matrix is nonsymmetric. All off-diagonal values must be specified.

The binary interaction parameters, $B_{i,j}$, have values of zero on the diagonal and the matrix is nonsymmetric. For each pair of species at least $A_{i,j}$ or $B_{i,j}$ should be specified.

The randomness parameters, $\alpha_{i,j}$, have values of zero on the diagonal and the matrix is symmetric. All off-diagonal values must be specified. Alternatively one can set the more generic form directly specifying parameter $\beta_{i,j}$ for which diagonal values are zero and the matrix is nonsymmetric. For each pair of species at least $\alpha_{i,j}$ or $\beta_{i,j}$ should be specified.

If any value for these parameters is missing in the database, it is set to zero (warning node is created).

$$A_{i,i} = 0 \tag{6-58}$$

$$B_{i,i} = 0 \tag{6-59}$$

$$\alpha_{i,i} = 0 \tag{6-60}$$

$$\alpha_{j,i} = \alpha_{i,j} \tag{6-61}$$

$$\tau_{i,i} = 0 \tag{6-62}$$

$$G_{i,i} = 1 \tag{6-63}$$

$$\beta_{i,i} = 0 \tag{6-64}$$

UNIQUAC

Abrams and Prausnitz followed up with another two-liquid model known as Universal Quasi Chemical equation (UNIQUAC) Ref. 21 which is formulated in terms of two activity coefficients:

$$\ln\gamma_i = \ln\gamma_{i,\text{comb}} + \ln\gamma_{i,\text{res}} \tag{6-65}$$

The first term is the combinatorial part contributes to the Gibbs free energy originating from size and shape effects as

$$\ln\gamma_{i,\text{comb}} = 1 - \phi_i + \ln\phi_i - \frac{z}{2}q_i\left(1 + \frac{\phi_i}{\theta_i} + \ln\left(\frac{\phi_i}{\theta_i}\right)\right) \tag{6-66}$$

and the second term is the residual part from chemical interactions between the molecules,

$$\ln\gamma_{i,\,\mathrm{res}} = q_i\left(1 - \ln\left(\frac{\sum_j x_j q_j \tau_{j,i}}{\sum_j x_j q_j}\right) - \sum_j \frac{x_j q_j \tau_{j,i}}{\sum_k x_j q_j \tau_{k,j}}\right) \tag{6-67}$$

where

$$\phi_i = \frac{r_i}{\sum_j x_j r_j} \tag{6-68}$$

$$\theta_i = \frac{q_i}{\sum_j x_j q_j} \tag{6-69}$$

$$\tau_{i,j} = \exp\left(\frac{-\Delta E_{i,j}}{T}\right) \tag{6-70}$$

The coordination number is taken equal to $z = 10$. The binary interaction energy parameters, $\Delta E_{i,j}$, are specified in terms of absolute temperature (K). The diagonal values are zero and the matrix is nonsymmetric. All off-diagonal values must be specified.

$$\Delta E_{i,i} = 0 \tag{6-71}$$

$$\tau_{i,i} = 1 \tag{6-72}$$

The volume parameters, r_i and surface area parameters, q_i are model-specific parameters for each species. If the parameters are not specified then they can be derived from the van der Waals volume, VVDW,i, and area, AVDW,i, respectively

$$r_i = \frac{V_{VDW,i}}{0.01517\times10^{-3}} \tag{6-73}$$

$$q_i = \frac{A_{VDW,i}}{2.5\times10^{5}} \tag{6-74}$$

For all species r_i or $V_{VDW,i}$ and q_i or $A_{VDW,i}$ must be specified.

UNIFAC

The UNIQUAC Functional-group Activity Coefficients (UNIFAC; see Ref. 22) uses the same equations as UNIQUAC but the parameters are constructed from group

contributions. The model can be used if UNIQUAC parameters are not available for all species. The activity coefficients are calculated from Equation 6-65. The combinatorial part follows from equation Equation 6-66, where

$$r_i = \sum_k \nu_{k,i} r_k \tag{6-75}$$

$$q_i = \sum_k \nu_{k,i} q_k \tag{6-76}$$

where r_k and q_k are the values for group k in species i, and$\nu_{k,i}$ is the number of occurrences of group k in molecule. The residual term in Equation 6-65 is calculated from a summation over functional groups:

$$\ln\gamma_{i,\text{res}} = \sum_k \nu_{k,i}(\ln\gamma_{k,\text{res}} - \ln\gamma_{i,k,\text{res}}) \tag{6-77}$$

The values for $\ln(\gamma_{k,\text{res}})$ are calculated from the mixture containing all species at a specified composition x. The values for $\ln(\gamma_{i,k,\text{res}})$ are calculated for a mixture of group k considering only pure species i. Both are defined, for functional group k, by

$$\ln\gamma_{k,\text{res}} = q_k\left(1 - \ln\left(\frac{\sum_l x_l q_l \tau_{l,k}}{\sum_l x_l q_l}\right) - \sum_j \frac{x_l q_l \tau_{k,l}}{\sum_m x_l q_l \tau_{m,l}}\right) \tag{6-78}$$

where x_l and x_m are the compositions of functional group l and m in the mixture

$$x_m = \frac{\sum_i x_i \nu_{m,i}}{\sum_{\cdot}\left(x_i \sum_{\cdot} \nu_{k,i}\right)} \tag{6-79}$$

For the calculation of a pure species' i residual activity we get:

$$x_m = \frac{\nu_{m,i}}{\sum_{\cdot} \nu_{k,i}} \tag{6-80}$$

The volume parameters r_k and surface area parameters q_k are model-specific parameters for each group. The binary interaction between groups k and m is

$$\tau_{k,m} = \exp\left(-\frac{A_{k,m}}{T}\right) \tag{6-81}$$

The binary interaction parameters, $A_{k,m}$, are specified in terms of absolute temperature. The diagonal values are zero, the matrix is nonsymmetric. All off-diagonal values must be specified.

The default group and interaction parameters are those published by the UNIFAC consortium (Ref. 23 through Ref. 28), with added groups from Balslev and Abildskov (Ref. 29) but can be modified per package or database. The groups must be specified for all species. Note that the interaction parameter matrix is sparse, and a package can only be used if all interaction parameters for all used groups are specified.

Chao Seader (Grayson-Streed)

The Chao-Seader model Ref. 15 correlates liquid phase partial coefficients for pure species, for use of hydrogen and hydrocarbon mixtures at elevated pressure and temperatures. It is expressed by

$$\ln\phi_{i,l} = \ln\gamma_i + \ln\phi_{i,l,0} \tag{6-82}$$

The activity is based on the Scatchard-Hildebrand equation Ref. 16 and presented in Equation 6-44 to Equation 6-46. Chao-Seader specific values for liquid volume, V_i and solubility parameter, δ_i are used.

If V_i is unspecified, it can be estimated by

- **a** molar volume at normal boiling point
- **b** van der Waals volume
- **c** from the Rackett model, Equation 6-79, at normal boiling point temperature.

If the Chao-Seader specific solubility parameter, δ_i, is not specified, the generic solubility parameter is used.

The fugacity coefficient for pure species i is correlated as

$$\log\phi_{i,l,0} = \log\phi_{i,l,1} + \omega_i \log\phi_{i,l,2} \tag{6-83}$$

$$\log\phi_{i,l,1} = A_{i,0} + \frac{A_{i,1}}{T_{r,i}} + A_{i,2}T_{r,i} + A_{i,3}T_{r,i}^2 + A_{i,4}T_{r,i}^3 \tag{6-84}$$
$$+(A_{i,7}T_{r,i}^2 + A_{i,6}T_{r,i} + A_{i,5})P_{r,i} + (A_{i,9}T_{r,i} + A_{i,8})P_{r,i}^2 \quad - \log P_{r,i}$$

$$\log\phi_{i,l,2} = A_{i,10} + \frac{A_{i,12}}{T_{r,i}} + A_{i,11}T_{r,i} + A_{i,13}T_{r,i}^3 + A_{i,14}(P_{r,i} - 0.6) \qquad (6\text{-}85)$$

A Chao-Seader specific acentric factor ω_i is used. If it is unknown, it can be set equal to the generic acentric factor. The parameter values are taken from the later publication of Grayson and Streed Ref. 17 and given in Table 6-1.

TABLE 6-1: CHAO-SEADER GRAYSON-STREED FUGACITY COEFFICIENT PARAMETERS.

	H_2	CH_4	OTHER		ALL
$A_{i,0}$	1.50709	1.36822	2.05135	$A_{i,10}$	-4.23893
$A_{i,1}$	2.74283	-1.54831	-2.10899	$A_{i,11}$	8.65808
$A_{i,2}$	-0.02110			$A_{i,12}$	-1.22060
$A_{i,3}$	0.00011	0.02889	-0.19396	$A_{i,13}$	-3.15224
$A_{i,4}$		-0.01076	0.02282	$A_{i,14}$	-0.02500
$A_{i,5}$	0.008585	0.10486	0.08852		
$A_{i,6}$		-0.02529			
$A_{i,7}$			-0.00872		
$A_{i,8}$			-0.00353		
$A_{i,9}$			0.00203		

The corresponding vapor phase model is Redlich-Kwong equation of state. The Chao-Seader (Grayson-Streed) model is valid when

- 255 K < T < 533 K
- P < 6.89 MPa
- P_r < 0.8
- 0.5 < $T_{r,i}$ < 1.3, for all hydrocarbons except CH_4
- x_{CH4} < 0.3
- For system that includes CH_4 or H_2S:

$$\sum_i x_i T_{r,i} < 0.93$$

The enthalpy, entropy and Gibbs free energy can be calculated from Equation 6-108 to Equation 6-117.

LIQUID VOLUME MODELS

When an activity coefficient model or the Chao-Seader (Grayson-Streed) model is used, a liquid volume model must be explicitly selected. It is also possible to assign a liquid volume model when an equation of state is used.

For liquids the density is defined as the reciprocal of the liquid volume:

$$\rho_l = \frac{1}{V_l} \tag{6-86}$$

Equation of State

When an equation of state is selected as the thermodynamic model, the liquid volume is calculated using the equation of state model. In the other cases, when the thermodynamic model is not an equation of state, an equation of state can be explicitly selected to calculate the liquid volume.

Note, when defining the equation of state for vapor and liquid systems, both phases must use the same equation of state.

Ideal Mixture

For an ideal mixture the liquid volume is computed from the pure species densities:

$$V_{l,m} = \sum_i \frac{x_i}{\rho_{i,l}} \tag{6-87}$$

The pure species densities are evaluated from the built-in database.

COSTALD

Hankinson and Thomson Ref. 30 presented the Corresponding States Liquid Density (COSTALD) equation as

$$\frac{V}{V_{mix}} = V_{r,ref}(1 - \omega V_{r,\delta}) \tag{6-88}$$

$$V_{r,ref} = 1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + c(1 - T_r) + d(1 - T_r)^{4/3} \tag{6-89}$$

$$V_{r,\delta} = \frac{e + fT_r + gT_r^2 + hT_r^3}{T_r - 1.00001} \tag{6-90}$$

$$V_{mix} = \frac{1}{4}\left(\sum_i x_i V_i + 3\left(\sum_i x_i V_i^{2/3}\right)\left(\sum_i x_i V_i^{1/3}\right)\right) \tag{6-91}$$

$$T_c = \frac{\left(\sum_i x_i \sqrt{T_{c,i} V_i}\right)}{V_{mix}} \tag{6-92}$$

$$T_r = \begin{cases} \dfrac{T}{T_c} & T < T_c \\ 1 & T \geq T_c \end{cases} \tag{6-93}$$

$$\omega = \sum_i x_i \omega_i \tag{6-94}$$

where the volume, V_i and acentric factor, ω_i for species i are model specific parameters. If the COSTALD volume parameter is unspecified, it is estimated from the van der Waals volume when $V_{VDW,i} > 0.3 \times 10^{-3}$ m^3/mol

$$V_i = 5.385\, V_{VDW,i} - 5.1022 V_{VDW,i}^2 + 79.524 V_{VDW,i}^3 - 99.316 V_{VDW,i}^4 + 100.88 V_{VDW,i}^5 - 1152.7 V_{VDW,i}^6 \tag{6-95}$$

otherwise it can be set equal to the critical volume as

$$V_i = V_{c,i} \tag{6-96}$$

If the COSTALD acentric factor, ω_i is not specified then it can be set equal to the generic acentric factor for species i. Critical temperature, $T_{c,i}$ must be specified for all species.

The correlation parameter values are:

TABLE 6-2: REDUCED VOLUME CORRELATION PARAMETERS IN COSTALD.

a	-1.52816	e	-0.296123
b	1.43907	f	0.386914
c	-0.81446	g	-0.0427258
d	0.190454	h	-0.0480645

Rackett

The Rackett equation Ref. 31 computes the liquid density at the saturation point, and can be used to describe liquid density at any pressure using the assumption that the liquid is incompressible. The equation and its condition can be expressed as:

$$V_l = \left(R\sum_i \frac{x_i T_{c,i}}{(MW)_i P_{c,i}}\right)\left(\sum_i Z_{r,i}\right)^{(1+(1-T_r^2)^{2/7})}\left(\sum_i x_i (MW)_i\right) \tag{6-97}$$

$$T_c = \sum_i x_i T_{c,i} \tag{6-98}$$

$$T_r = \begin{cases} \dfrac{T}{T_c} & T < T_c \\ 1 & T \geq T_c \end{cases} \tag{6-99}$$

Critical temperatures, $T_{c,i}$, critical pressures, $P_{c,i}$, and molecular weights, M_i, must be specified for all species. The model parameter, $Z_{r,i}$, must be specified for all species. If the value is not available it can be set to the critical compressibility factor:

$$Z_{r,i} = Z_{c,i} \tag{6-100}$$

Selecting the Right Thermodynamic Model

There are methods to choose the appropriate thermodynamic models; see Ref. 78. This choice depends on the nature of the property, composition of the mixture, operational pressure and temperature, and availability of model's parameters for the

simulation; see Ref. 79. Below is a decision tree that can be used as a guide for choosing the thermodynamic model:

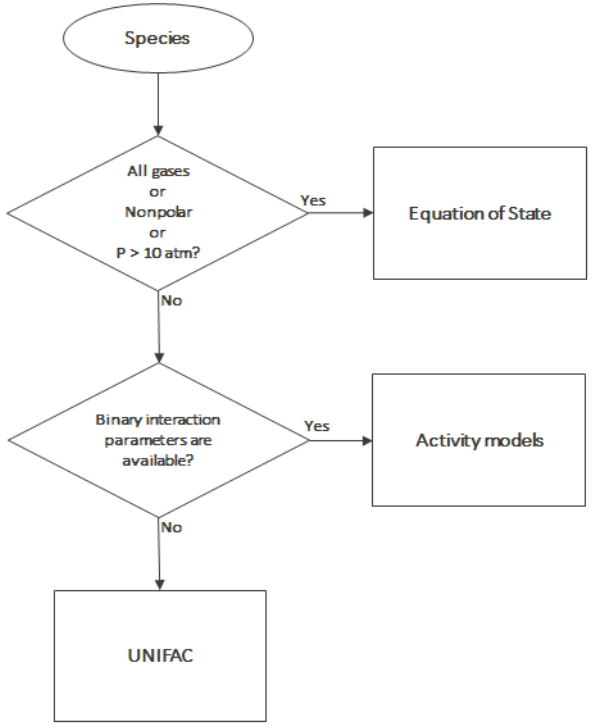


Figure 6-36: Decision tree to select thermodynamics model.

It is possible to manually modify the species properties, such as parameters and temperature-dependent functions, in the database file. In the same manner, you can manually add new species that do not exist in the database. To do this, right-click a system node under **Thermodynamics** and select **Export thermodynamic system**. Save the thermodynamic system as an xml file.

All the parameters and temperature-dependent properties are saved inside a `<Compound CompID="name"></Compound>` block. For example, to edit the acentric factor of methane from 0.01141 to 0.2 perform the following steps

- Open the saved xml file for the thermodynamic system
- Find the compound methane which starts with the line:

  `<Compound CompID="methane">`

- Find the line with the acentric factor and change it to

  `<AcentricFactor >0.2</AcentricFactor>.`

To use the system with the updated species, right-click the Thermodynamics node and select Import System.

For temperature-dependent functions, for example for the (saturated) liquid density, the database input is of the form:

```
<Density>
   <Phase>Liquid</Phase>
   <Coefficients>Tlb;a0;a1;a2;a3;Tub</Coefficients>
   <Data>Tlb;f(Tlb);Tub;f(Tub)</Data>
<Comment></Comment>
</Density>
```

Here T_{lb} and T_{ub} defines the lower and upper bound for a temperature range, and a_1 to a_4 are the corresponding coefficients for a cubic polynomial as $f(T) = a_0 + a_1T + a_2T^2 + a_3T^3$ fitted for that range. Multiple sequential ranges can be added by appending temperature ranges and coefficient sets. The `<Data></Data>` block can be used to input data points directly.

The unit for temperature is K. The unit used for the temperature dependent properties (fitted polynomials functions) are defined in the table below:

TABLE 6-3: UNIT FOR TEMPERATURE-DEPENDENT PROPERTIES.

PROPERTY	UNIT
Liquid density	mol/m^3
Ideal heat capacity	J/mol/K
Ln vapor pressure	1
Heat of vaporization	J/mol
Vapor viscosity	Pa·s
Ln liquid viscosity	1
Vapor thermal conductivity	W/m/K
Liquid thermal conductivity	W/m/K
Surface tension	N/m

Species Property References

All references used for the included constants and temperature-dependent properties are available in the database file. In the xml file these are defined with the in line tag `Comment` for constants. For example the critical pressure of methane is defined as

```
<CriticalPressure Comment="Twu C.H. et al.  Fluid Phase Equilibria
105 (1995) 49-59.">4604005.35</CriticalPressure>.
```

citing the work of Twu and others(Ref. 8).

For temperature-dependent properties a separate `<Comment></Comment>` block is used.

The reference comments can be inspected in the settings window by right-clicking a species property node (under a **Thermodynamic System**) and selecting **Properties**.

Thermodynamic Properties Definitions

The thermodynamic properties provided are listed as species and mixture property in a Property package.

Ideal Gas

The ideal gas law is independent of composition and determines V at given T and P. Density can be calculated from

$$\rho = \frac{1}{V} \tag{6-101}$$

The partial fugacity coefficients

$$\ln\hat{\phi}_i = 0 \tag{6-102}$$

The ideal gas enthalpy for mixture

$$H_{ig} = \sum_i x_i \left(H_{i,ig,T_{ref}} + \int_{T_{ref}}^{T} C_{P,i,ig} dT \right) \tag{6-103}$$

where $H_{i,ig,T\text{ref}}$ relates the enthalpy of an ideal gas to the enthalpy at the selected reference state for species i.

The ideal gas entropy for species i

$$S_{ig} = \sum_i x_i \left(S_{i,ig,T_{ref}} - R\ln x_i + \int_{T_{ref}}^{T} \frac{C_{P,i,ig}}{T} dT \right) - R\ln\left(\frac{P}{P_{\text{ref}}}\right) \tag{6-104}$$

where $S_{i,ig,T\text{ref}}$ is the entropy of an ideal gas to the entropy of species at the selected reference state.

The Gibbs free energy follows from

$$G_{ig} = H_{ig} - TS_{ig} \tag{6-105}$$

Equation of State

The equation of state determines V at given x, T, and P. Density can be expressed as Equation 6-101. The partial fugacity coefficients are derived from

$$\ln\hat{\phi}_i = \frac{1}{RT}\int_0^P \left(\hat{V}_i - \frac{RT}{P}\right) \tag{6-106}$$

where V_i is the partial molar volume. The enthalpy, entropy, and Gibbs free energy follow from the partial fugacity coefficients and the ideal gas contributions as:

$$H = H_{ig} - RT^2 \sum_i x_i \left(\frac{\partial \ln\hat{\phi}_i}{\partial T}\right) \tag{6-107}$$

$$S = S_{ig} - R\sum_i x_i \left(\ln\hat{\phi}_i + T\frac{\partial \ln\hat{\phi}_i}{\partial T}\right) \tag{6-108}$$

$$G = G_{ig} - RT\sum_i x_i \ln\hat{\phi}_i \tag{6-109}$$

Heat Capacity

Heat capacity at constant pressure is calculated from

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{\mathrm{P,x}} \tag{6-110}$$

It is available when enthalpy is available. Heat capacity at constant volume is defined by

$$C_v = \left(\frac{\partial H}{\partial T}\right)_{\mathrm{v,x}} \tag{6-111}$$

The relationship between heat capacity at constant pressure and constant volume can be expressed as:

$$C_p - C_v = T\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P,x}} \left(\frac{\partial P}{\partial T}\right)_{\mathrm{v,x}} \tag{6-112}$$

were v is a function of T and P. A Taylor expansion of $v$at constant composition gives

$$\Delta v = \left(\frac{\partial V}{\partial T}\right)_{\mathrm{P,x}} \Delta T + \left(\frac{\partial V}{\partial P}\right)_{\mathrm{T,x}} \Delta P = 0 \tag{6-113}$$

Rearranging equations above gives

$$C_{\mathrm{v}} = C_{\mathrm{P}} + \frac{T\left(\frac{\partial V}{\partial T}\right)^2_{\mathrm{P,x}}}{\left(\frac{\partial V}{\partial P}\right)_{\mathrm{T,x}}} \tag{6-114}$$

C_v is available if C_p and volume are available and fluid is compressible by means of volume is pressure dependent. For ideal gas Equation 6-112 express as

$$C_p - C_v = R \tag{6-115}$$

Specific heat capacity ratio is defined as

$$\Upsilon = \frac{C_p}{C_v} \tag{6-116}$$

Activity Coefficient Models

The enthalpy, entropy, and Gibbs free energy follow from the activity coefficients and the ideal gas contributions in Equation 6-103 – Equation 6-105. The activity coefficients describe the deviation of chemical potentials from the ideal liquid phase, so heats of vaporization need to be accounted for

$$H = \sum_i x_i \left(H_{i,\,ig,\,T_{ref}} + \int_{T_{ref}}^{T} C_{P,\,i,\,ig} dT - \Delta H_{i,\,vap} - RT^2 \frac{\partial \ln \gamma_i}{\partial T} - RT^2 \frac{\partial \ln \hat{\phi}_{i,\,sat}}{\partial T} \right) \tag{6-117}$$

$$S = \sum_i x_i \left(S_{i,\,ig,\,T_{ref}} - R \ln x_i + \int_{T_{ref}}^{T} \frac{C_{P,\,i,\,ig}}{T} dT - R \ln \left(\frac{P_{i,\,sat}}{P_{ref}} \right) + \ln \gamma_i + T \frac{\partial \ln \gamma_i}{\partial T} + \ln \hat{\phi}_{i,\,sat} + T \frac{\partial \ln \hat{\phi}_{i,\,sat}}{\partial T} + R \frac{\Delta H_{i,\,vap}}{T} \right) \tag{6-118}$$

$$G = \sum_i x_i \left(H_{i,ig,T_{ref}} + \int_{T_{ref}}^{T} C_{P,i,ig} dT - T \left(S_{i,ig,T_{ref}} + \int_{T_{ref}}^{T} \frac{C_{P,i,ig}}{T} dT \right) + RT \left(\ln x_i + \ln \gamma_i + \ln \hat{\phi}_{i,sat} + \ln \frac{P_{i,sat}}{P_{ref}} \right) \right) \tag{6-119}$$

Note that if the vapor phase is ideal, then the saturated fugacity, $\phi_{i,sat}$, contribution can be ignored.

Other Properties

Partial fugacity is calculated from

$$\hat{f}_i = x_i \hat{\phi}_i P \tag{6-120}$$

Internal energy is calculated from

$$U = H - PV + \sum_i x_i U_{i,ig,ref} \tag{6-121}$$

where $U_{i,ig,ref}$ is the enthalpy of an ideal gas to the species enthalpy at the selected reference state.

Helmholts energy is calculated from

$$A = U - TS = G - PV \tag{6-122}$$

K-values for phases p and q are taken from

$$K_{i,p,q} = \frac{\hat{\phi}_{i,q}}{\hat{\phi}_{i,p}} \tag{6-123}$$

If only liquid phases are defined, the K-value calculation is reduced to

$$K_{i,p,q} = \frac{\gamma_{i,q}}{\gamma_{i,p}} \tag{6-124}$$

$$M_{mix} = \sum_i x_i M_i \tag{6-125}$$

Standard Enthalpy of Formation and Absolute Entropy Terms

Formation terms are not included in the enthalpy, entropy, or the internal energy. If the enthalpy of formation is specified for all species, EnthalpyF (H_F) represent the enthalpy including the formation terms. If the absolute entropy of all species are specified then the EntropyF (S_F) includes the absolute entropy.

At reference conditions, the heat of any reaction relates to the heat of formation as

$$\Delta H_{reac,\,ref} = \sum_i \nu_i (\Delta H_{f,\,ref}) \tag{6-126}$$

Note that for reacting flow or a heat balance in a reactor when the heat of reaction is explicitly taken into account, the enthalpy should not include the heat of formation.

The following enthalpy expression should be used:

$$H_F = H + \sum_i x_i \Delta H_{f,\,i,\,ref} \tag{6-127}$$

$H_{f,i,\mathrm{ref}}$ is calculated such that it matches the reference state of the package, even if the species have a different reference state. Similarly, the absolute entropy of each species is taken into account according to

$$S_F = S + \sum_i x_i S_{abs,\,i} \tag{6-128}$$

The entropy balance over a process that includes reactions should include either the entropy of reaction and use S, or use S_F without entropy of reaction.

In database, a set of parameters introduced to define Absolute entropy and Standard enthalpy of formation for ideal gas and different phases (Vapor, liquid, Solid, and Aqueous infinite dilution). One can use these parameters to calculate Gibbs free energy of reaction when different phases are available (See Electrode reaction).

SPECIES GIBBS FREE ENERGY OF FORMATION

As the COMSOL ThermoDB does not include entropy of formation of species, entropy Equation 6-128 and in consequence Gibbs free energy Equation 6-109 are estimated from absolute entropy's value. Therefore, the absolute value of entropy of formation and Gibbs free energy of formation of the species are not correct. However, for our applications these absolute values are not required while the value of entropy and Gibbs free energy change of reaction (the difference value) are correct.

If user needs the absolute value of entropy of formation, it is possible to estimate it by:

$$S_i = \Delta S_{f,i} = \sum_j \nu_j S_{abs,j} \tag{6-129}$$

where the entropy of formation of species *i* is calculated from its elemental constituent *j*. For example, entropy of formation of ammonia at 298 K is

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3 \tag{6-130}$$

$$\Delta S_{f,NH_3} = 2S_{abs,NH_3} - (S_{abs,N_2} + 3S_{abs,H_2}) \tag{6-131}$$

The values from RHS of Equation 6-131 can be extracted from COMSOLThermoDB. This value should be used in Equation 6-127 to estimate the absolute value of Gibbs free energy of species.

Reference State

The reference temperature, pressure and phase can be specified for each package and for species within a package. The reference phase can be a real phase or an ideal gas. If a reference temperature, pressure, or phase is unspecified for a particular species, the package reference temperature, pressure, or phase is used for that species.

The reference values for enthalpy, $H_{i,ref}$, entropy, $S_{i,ref}$, and internal energy, $U_{i,ref}$, are calculated so that the pure species enthalpy, entropy, and internal energy are equal to zero at reference conditions.

The reference values for enthalpy, including formation terms, and entropy, including absolute terms, are calculated such that the corresponding property for pure species *i* has a value equal to the specified formation term at the species reference conditions.

Transport Properties

This section includes definitions of the models available in for thermal conductivity, viscosity, and diffusivity:

- Thermal Conductivity
- Viscosity
- Diffusivity

THERMAL CONDUCTIVITY

Vapor

Ideal

The thermal conductivity correlations is according to:

$$\lambda_v = \sum_i x_i \lambda_{i,v} + \Delta\lambda_{v,P} \tag{6-132}$$

The pressure correction $\Delta\lambda_{v,P}$ is calculated from the method of Stiel and Thodos, see Ref. 32, which is applicable for $\rho_r<3$, but is less accurate for H_2, strongly polar gases, and gases with a high degree of hydrogen bonding, such as H_2O and NH_3

$$\Delta\lambda_{v,P} = \frac{P_c^{2/3}}{\sqrt{M}T_c^{1/6}Z_c^5} A(\exp((B\rho_r)+C)) \tag{6-133}$$

$$\rho_r = \frac{\rho}{\rho_c} \tag{6-134}$$

$$\rho_c = \frac{1}{V_c} \tag{6-135}$$

The mixing rules are as suggested by Yorizane, see Ref. 33:

$$V_c = \sum_i x_i \sum_j x_j V_{c,i,j} \tag{6-136}$$

$$T_c = \frac{\sum_i x_i \sum_j x_j V_{c,i,j} T_{c,i,j}}{V_c} \tag{6-137}$$

$$\omega = \sum_i x_i \omega_i \tag{6-138}$$

$$Z_c = 0.291 - 0.08\omega \tag{6-139}$$

$$P_c = \frac{RT_cZ_c}{V_c} \tag{6-140}$$

$$M = \sum_i x_i M_i \tag{6-141}$$

where the binary constants are

$$V_{c,i,j} = \frac{1}{8}(V_{c,i}^{1/3} + V_{c,j}^{1/3})^3 \tag{6-142}$$

$$T_{c,i,j} = \sqrt{T_{c,i} T_{c,j}} \tag{6-143}$$

The Stiel and Thodos coefficients are

TABLE 6-4: PRESSURE CORRECTION PARAMETERS.

	A	B	C
$\rho_r < 0.5$	A_1=2.702×10^8	B_1=0.535	C_1=-1
$0.5 \le \rho_r < 2.0$	A_2=2.528×10^8	B_2=0.670	C_2=-1.069
$\rho_r \ge 2.0$	A_3=0.574×10^8	B_3=1.155	C_3= 2.016

However, in order to ensure 0^{th}-order continuity at $\rho_r = 0.5$ and $\rho_r = 2.0$, the following coefficients for $0.5 \le \rho_r < 2.0$ are recalculated from

$$A_2 = -\frac{A_1 C_1 + A_1 \exp(0.5\ B_1) - A_3 C_3 - A_3 \exp(2.0\ B_3)}{\exp(2.0\ B_2) - \exp(0.5\ B_1)} \tag{6-144}$$

$$C_2 = -\frac{A_1 C_1 \exp(2.0\ B_2) + A_1 \exp(0.5\ B_1)\exp(2.0\ B_2)}{A_1 C_1 + A_1 \exp(0.5\ B_1) - A_3 C_3 - A_3 \exp(2.0\ B_3)} - \frac{A_3 C_3 \exp(2.0\ B_2) + A_3 \exp(0.5\ B_2)\exp(2.0\ B_3)}{A_1 C_1 + A_1 \exp(0.5\ B_1) - A_3 C_3 - A_3 \exp(2.0\ B_3)} \tag{6-145}$$

The vapor thermal conductivity correlation must be available for all species. Also critical volumes, $V_{c,i}$, critical temperatures, $T_{c,i}$, molecular weights M_i, and acentric factors ω_i must be specified for all species.

Kinetic Theory

Lindsay and Bromley (see Ref. 34) provided an equation for the interaction parameters of the method of Wassiljewa (see Ref. 35) based on the kinetic theory, to provide mixture thermal conductivity from pure species values

$$\lambda_v = \sum_i \left(\frac{x_i \lambda_{i,v}}{\sum_j x_j \lambda \phi_{i,j}} \right) + \Delta\lambda_{v,P} \tag{6-146}$$

$$\phi_{i,j} = \frac{1}{4}\left(1 + \sqrt{\frac{\eta_{i,v}}{\eta_{j,v}}\left(\frac{M_j}{M_i}\right)^{3/4}\left(\frac{T + \left(\frac{3}{2}\right)T_{b,i}}{T + \left(\frac{3}{2}\right)T_{b,j}}\right)}\right)^2 \left(\frac{T + \sqrt{\left(\frac{9}{4}\right)T_{b,i}T_{b,j}}}{T + \left(\frac{3}{2}\right)T_{b,i}} \right) \tag{6-147}$$

where the pressure correction $\Delta\lambda_{v,P}$ is calculated from Equation 6-133. Both vapor thermal conductivity correlation $\lambda_{i,v}$ and the vapor viscosity correlation $\eta_{i,v}$ must be available for all species. In addition, all normal boiling points $T_{i,b}$, molecular weights M_i, critical volumes $V_{c,i}$, critical temperatures $T_{c,i}$, and acentric factors ω_i must be specified.

Water (IAPWS)

The International Association of the Properties of Water and Steam recommend an equation Ref. 36 which is valid in the following range:

$$273.15\ \text{K} \le T \le 773.15\ \text{K} \qquad p \le 100\ \text{MPa} \tag{6-148}$$

$$773.15\ \text{K} \le T \le 923.15\ \text{K} \qquad p \le 70\ \text{MPa} \tag{6-149}$$

$$923.15\ \text{K} \le T \le 1073.15\ \text{K} \qquad p \le 40\ \text{MPa} \tag{6-150}$$

Liquid

The following mixture models are available for liquid thermal conductivity

Ideal

To calculate the mixture liquid thermal conductivity, $\lambda_{l,m}$, the values of pure liquid thermal conductivity correlations are mixed ideally

$$\lambda_{l,m} = \sum_i x_i \lambda_{i,l} \tag{6-151}$$

The pressure dependence is based on the work of Missenard (Ref. 52) where

$$\frac{\lambda_{l,m,P}}{\lambda_{l,m}} = 1 + Q P_r^{0.7} \tag{6-152}$$

where Q is correlated as

$$Q = -0.013693477 + 0.057427673T_r + 0.001617831(T_r)(\ln P_1) \quad (6\text{-}153)$$

and the following mixing rules are used

$$T_r = \frac{T}{T_c} \quad (6\text{-}154)$$

$$P_r = \frac{P}{P_c} \quad (6\text{-}155)$$

$$P_c = \frac{RT_cZ_c}{V_c} \quad (6\text{-}156)$$

$$V_c = \sum_i x_i V_{c,i} \quad (6\text{-}157)$$

$$T_c = \sum_i x_i T_{c,i} \quad (6\text{-}158)$$

$$Z_c = \sum_i x_i Z_{c,i} \quad (6\text{-}159)$$

All liquid thermal conductivity correlations must be specified. All values for critical temperatures, $T_{c,i}$, critical volumes, $P_{c,i}$ and critical compressibility factors, $Z_{c,i}$ must be specified for all species i.

Power Law

The values of pure liquid vapor thermal conductivity correlations are mixed according to the following power law

$$\frac{1}{\lambda_{l,m}^2} = \sum_i \frac{x_i}{\lambda_{l,i}} \quad (6\text{-}160)$$

All liquid thermal conductivity correlations must be specified. The model is valid for pure compound thermal conductivity values that are no more apart than a factor of 2 (Ref. 53 and Ref. 54). The pressure dependence is introduced using Equation 6-152 through Equation 6-159. All values for critical temperatures, $T_{c,i}$, critical volumes, $P_{c,i}$ and critical compressibility factors, $Z_{c,i}$ must be specified for all spices i.

Local Composition

The local composition model by Rowley (Ref. 54) uses an ideal and excess contribution

$$\lambda_{l,\,m} = \lambda_{l,\,\text{ideal}} + \lambda_{l,\,\text{excess}} \tag{6-161}$$

The ideal part is based on mass fractions

$$\lambda_{l,\,\text{ideal}} = \sum_i \omega_i \lambda_{i,\,l} \tag{6-162}$$

$$\omega_i = \frac{x_i M_i}{\sum_j x_j M_j} \tag{6-163}$$

The excess term is based on NRTL local concentrations

$$\lambda_{l,\,\text{excess}} = \frac{\sum_i \sum_j \omega_i \omega_j G_{j,\,i} (\lambda_{j,\,i} - \lambda_{i,\,l})}{\sum_j \omega_j G_{j,\,i}} \tag{6-164}$$

where $G_{j,i}$ follows from Equation 6-57. The binary interaction terms follow from

$$\lambda_{i,\,j} = \lambda_{j,\,i} = \frac{\bar{\omega}_i \bar{\omega}_{i,\,i} \lambda_{i,\,l} + \bar{\omega}_j \bar{\omega}_{j,\,j} \lambda_{j,\,l}}{\bar{\omega}_i \bar{\omega}_{i,\,i} + \bar{\omega}_j \bar{\omega}_{j,\,j}} \tag{6-165}$$

which is symmetric, and on the diagonal,

$$\lambda_{i,\,i} = \lambda_{i,\,l} \tag{6-166}$$

and

$$\bar{\omega}_{i,\,i} = \bar{\omega}_i (\bar{\omega}_i + \bar{\omega}_j G_{j,\,i}) \tag{6-167}$$

with $\bar{\omega}_i$ is the composition in the binary mixture of species i and j and the local composition is equi-molar

$$\bar{\omega}_i = \frac{M_i \sqrt{G_{j,\,i}}}{M_i \sqrt{G_{j,\,i}} + M_j \sqrt{G_{i,\,j}}} \tag{6-168}$$

All liquid thermal conductivity correlations must be specified. The pressure dependence is introduced using Equation 6-152 – Equation 6-159. All values for critical temperatures $T_{c,i}$, critical volumes $P_{c,i}$, critical compressibility factors $Z_{c,i}$, and molecular weights M_i must be specified for all compounds i. In addition, all NRTL binary interaction parameters $A_{i,j}$ must be specified. Unspecified values for NRTL interaction parameters $B_{i,j}$ are set to zero. The randomness parameters $\alpha_{i,j}$ have values of zero on the diagonal and the matrix is symmetric. All off-diagonal values must be specified. NRTL model is presented in Equation 6-53 to Equation 6-64.

Local Composition (Modified)

Rowley (Ref. 53) adapted the local composition model by replacing the mixing rule in Equation 6-165 by the following

$$\lambda_{i,j} = \lambda_{j,i} = \frac{M_i(\bar{\omega}_i\bar{\omega}_{i,i})\lambda_{i,l} + M_j(\bar{\omega}_j\bar{\omega}_{j,j})\lambda_{j,l}}{M_i(\bar{\omega}_i\bar{\omega}_{i,i}) + M_j(\bar{\omega}_j\bar{\omega}_{j,j})} \tag{6-169}$$

which he found to produce better model predictions in most cases where both the Local Composition model and Power Law model have trouble. However, the model is not as generally applicable; for instance, systems containing H_2O are not well described by this model due to the low molecular weight of H_2O.

Water (IAPWS)

The International Association of the Properties of Water and Steam recommend an equation Ref. 36 which is valid in the following range:

$$273.15\ \text{K} \le T \le 773.15\ \text{K} \qquad p \le 100\ \text{MPa} \tag{6-170}$$

$$773.15\ \text{K} \le T \le 923.15\ \text{K} \qquad p \le 70\ \text{MPa} \tag{6-171}$$

$$923.15\ \text{K} \le T \le 1073.15\ \text{K} \qquad p \le 40\ \text{MPa} \tag{6-172}$$

VISCOSITY

Vapor

Wilke

Wilke, see Ref. 37, based his method for mixture viscosity of the vapor phase on kinetic theory:

$$\eta_v = \sum_i \left(\frac{x_i \eta_{i,v}}{\sum_j x_j \psi_{i,j}} \right) \tag{6-173}$$

$$\psi_{i,j} = \frac{\left(1 + \sqrt{\frac{\eta_{i,v}}{\eta_{j,v}}} \left(\frac{M_j}{Mi} \right)^{1/4} \right)^2}{\sqrt{8\left(1 + \frac{M_i}{M_j} \right)}} \tag{6-174}$$

The vapor viscosity correlation $\eta_{i,v}$ must be available for all species. In addition, all molecular weights M_i must be specified.

Brokaw

Brokaw (see Ref. 38) uses the same basic equation as Wilke (Equation 6-173). However, Equation 6-174 is replaced by

$$\psi_{i,j} = S_{i,j} A_{i,j} \sqrt{\frac{\eta_{i,v}}{\eta_{j,v}}} \tag{6-175}$$

and the interaction parameter is defined as

$$A_{i,j} = \frac{\beta_{i,j}}{\sqrt{RM_{i,j}}} \left(1 + \frac{RM_{i,j} - RM_{i,j}^{0.45}}{2(1 + RM_{i,j}) + \frac{1 + RM_{i,j}^{0.45}}{(\sqrt{\beta_{i,j}})(1 + RM_{i,j})}} \right) \tag{6-176}$$

where

$$\beta_{i,j} = \left(\frac{4 M_i M_j}{(M_i + M_j)^2} \right)^{1/4}, \quad RM_{i,j} = \frac{M_i}{M_j} \tag{6-177}$$

The vapor viscosity correlation, $\eta_{i,v}$ must be available for all species i. In addition, all molecular weights M_i must be specified. If Lennard-Jones energy ε_i (see Ref. 39) Stockmayer's polar parameter $\delta_{s,i}$(Ref. 40 and Ref. 41) are specified for both species i and j then

$$S_{i,j} = \frac{1 + \sqrt{\frac{T^2}{\varepsilon_i \varepsilon_j}} + \frac{1}{4}\delta_{s,i}\delta_{s,j}}{\sqrt{1 + \frac{T}{\varepsilon_i} + \frac{1}{4}\delta_{s,i}}\sqrt{1 + \frac{T}{\varepsilon_j} + \frac{1}{4}\delta_{s,j}}} \tag{6-178}$$

Otherwise,

$$S_{i,j} = 1 \tag{6-179}$$

High Pressure Modification

To account for the effect of pressure on vapor viscosity, a pressure correction can be applied. The pressure dependence is based on kinetic gas theory, which adds the following term to the vapor viscosity:

$$\Delta\eta_{v,P} = \left(\frac{\sqrt{M_t}P_c^{2/3}}{T_c^{1/6}}\right)\left(\frac{10^{-7}}{101325^{2/3}}\zeta\right) \tag{6-180}$$

where ξ is calculated from the correlation of Jossi (Ref. 42), which is applicable for $\rho_r < 3.0$. It is less accurate for H_2, strongly polar gases and gases with a high degree of hydrogen bonding such as H_2O and NH_3.

The correction factor is due to using pressure, atm, and viscosity, cP, units in Jossi's correlation. It is expressed as:

$$(\xi + 1)^{\frac{1}{4}} = 1.0230 + 0.23364\rho_r + 0.58533\ \rho_r^2 \tag{6-181}$$

$$- 0.40758\ \rho_r^3 + 0.093324\ \rho_r^4$$

$$\rho_r = \frac{\rho}{\rho_c} \tag{6-182}$$

$$\rho_c = \frac{1}{V_c} \tag{6-183}$$

The following mixture rules are used

$$P_c = \frac{RT_cZ_c}{V_c},\ V_c = \sum_i x_i V_{c,i},\ T_c = \sum_i x_i T_{c,i} \tag{6-184}$$

$$Z_c = \sum_i x_i Z_{c,i}, \; M_t = \sum_i x_i M_i \tag{6-185}$$

The values for critical volumes, $V_{c,i}$, critical temperatures, $T_{c,i}$, critical compressibility factors, $Z_{c,i}$ and molecular weights, M_i must be specified for all species i.

The high pressure correction is available for the Wilke and Brokaw mixture models. The vapor viscosity follows from

$$\eta_v = \eta_{v,\,\text{Wilke}} + \Delta\eta_{v,\,P} \tag{6-186}$$

where $\eta_{v,\text{Wilke}}$ is calculated from Equation 6-173.

Pedersen Corresponding States Model

The corresponding states viscosity model of Pedersen (Ref. 43 and Ref. 44) applies to both vapor and liquid phases of hydrocarbon mixtures. The selected reference species is CH_4.

The CH_4 viscosity is calculated from Ref. 45, modified by Pedersen and Fredunsland (Ref. 46) to avoid issues below 91 K where CH_4 becomes solid

$$\eta_{CH_4} = \eta_{CH_4,\,0} + \rho_{CH_4}\eta_{CH_4,\,1} + F_1\eta_{CH_4,\,2} + F_2\eta_{CH_4,\,3} \tag{6-187}$$

where

$$F_1 = \frac{H+1}{2} \tag{6-188}$$

$$F_1 = \frac{1-H}{2} \tag{6-189}$$

$$H = \frac{\exp(\Delta T) - \exp(-\Delta T)}{\exp((\Delta T) + \exp(-\Delta T))} \tag{6-190}$$

$$\Delta T = T - 91 \qquad (T \in K) \tag{6-191}$$

Here, ρ_{CH4} is used in g/cm^3; for the mass-mole conversion of ρ_{CH4}, a molecular weight of M_{CH4} = 16.042568 g/mol is used.

The dilute gas part is given by

$$\eta_{CH_4,0} = \frac{-L_1}{T} + \frac{L_2}{T^{2/3}} - \frac{L_3}{T^{1/3}} + L_4 - L_5 T^{1/3} + L_6 T^{2/3} - L_7 T + L_8 T^{4/3} - L_9 T^{5/3} \tag{6-192}$$

The first density correction for the moderately dense gas is given by

$$\eta_{CH_4,1} = L_{10} - L_{11}\left(1.4 - \ln\frac{T}{168}\right)^2 \tag{6-193}$$

The remainder is given by the empirical correlation

$$\eta_{CH_4,2} = \exp\left(\frac{L_{12}}{T} - L_{13}\right)\left(\exp\left((\sqrt[10]{\rho_{CH_4}})\left(L_{14} - \frac{L_{15}}{T^{3/2}}\right) + \left(\frac{\rho_{CH_4} - \rho_{c,CH_4}}{\rho_{c,CH_4}}\right)(\sqrt{\rho_{CH_4}})\left(L_{16} + \frac{L_{17}}{T} + \frac{L_{18}}{T^2}\right)\right) - 1\right) \tag{6-194}$$

The correction term for solid CH_4

$$\eta_{CH_4,3} = \exp\left(\frac{L_{19}}{T} - L_{20}\right)\left(\exp\left((\sqrt[10]{\rho_{CH_4}})\left(L_{21} - \frac{L_{22}}{T^{3/2}}\right) + \left(\frac{\rho_{CH_4} - \rho_{c,CH_4}}{\rho_{c,CH_4}}\right)(\sqrt{\rho_{CH_4}})\left(L_{23} + \frac{L_{24}}{T} + \frac{L_{25}}{T^2}\right)\right) - 1\right) \tag{6-195}$$

with the values of the parameters L_1 through L_{25} are listed in Table 6-5 below:

TABLE 6-5: METHANE VISCOSITY NUMERICAL COEFFICIENTS.

L_1	$2.090975 \cdot 10^5$	L_{10}	1.696985927	L_{19}	9.74602
L_2	$2.647269 \cdot 10^5$	L_{11}	0.133372346	L_{20}	44.6055
L_3	$1.472818 \cdot 10^5$	L_{12}	188.73011594	L_{21}	18.0834
L_4	47167.40	L_{13}	10.35060586	L_{22}	4126.66
L_5	9491.827	L_{14}	17.571599671	L_{23}	0.976544
L_6	1219.979	L_{15}	3019.3918656	L_{24}	81.8134
L_7	96.27993	L_{16}	0.042903609488	L_{25}	15649.9
L_8	4.274152	L_{17}	145.29023444		
L_9	0.08141531	L_{18}	6127.6818706		

Here, ρ_{CH4} is used in g/cm^3; the critical density is given by $\rho_{c,CH4} = 0.16284$ g/cm^3. The following equation by McCarty (Ref. 47) is solved for the density of CH_4

$$P = N_1\rho_{CH_4}T + \rho_{CH_4}^2\left(-N_2T + N_3\sqrt{T} - N_4 + \frac{N_5}{T} - \frac{N_6}{T^2}\right) \tag{6-196}$$
$$+ \rho_{CH_4}^3\left(N_7T - N_8 + \frac{N_9}{T} - \frac{N_{10}}{T^2}\right) + \rho_{CH_4}^4\left(-N_{11}T + N_{12} + \frac{-N_{13}}{T}\right) + N_{14}\rho_{CH_4}^5$$
$$+ \rho_{CH_4}^6\left(-\frac{N_{15}}{T} + \frac{N_{16}}{T^2}\right) + N_{17}\frac{\rho_{CH_4}^7}{T} + \rho_{CH_4}^8\left(\frac{N_{18}}{T} + \frac{N_{19}}{T^2}\right) + N_{20}\frac{\rho_{CH_4}^9}{T}$$
$$+ \exp(-N_{21}\rho_{CH_4}^2)\left(\rho_{CH_4}^3\left(\frac{N_{22}}{T^2} - \frac{N_{23}}{T^3}\right) + \rho_{CH_4}^5\left(\frac{N_{24}}{T^2} + \frac{N_{25}}{T^4}\right) + \rho_{CH_4}^7\left(\frac{N_{26}}{T^2} + \frac{N_{27}}{T^3}\right)\right.$$
$$\left. + \rho_{CH_4}^9\left(-\frac{N_{28}}{T^2} - \frac{N_{29}}{T^4}\right) + \rho_{CH_4}^{11}\left(-\frac{N_{30}}{T^2} + \frac{N_{31}}{T^3}\right) + \rho_{CH_4}^{13}\left(\frac{N_{32}}{T^2} - \frac{N_{33}}{T^3} + N_{34}T^4\right)\right)$$

where ρ_{CH4} is used in mol/l.

TABLE 6-6: COEFFICIENTS IN THE FUNCTIONAL FORM OF THE MCCARTY EOS.

N_1	0.08205616	N_{13}	2.8685285973	N_{25}	$1.6428375992\cdot10^{6}$
N_2	0.018439486666	N_{14}	$0.11906973942\cdot10^{-3}$	N_{26}	0.21325387196
N_3	1.0510162064	N_{15}	0.0085315715699	N_{27}	37.791273422
N_4	16.057820303	N_{16}	3.8365063841	N_{28}	$0.1185701681\cdot10^{-4}$
N_5	848.44027562	N_{17}	$0.24986828379\cdot10^{-4}$	N_{29}	31.630780767
N_6	42738.409106	N_{18}	$0.57974531455\cdot10^{-5}$	N_{30}	$0.4100678294\cdot10^{-5}$
N_7	$0.76565285254\cdot10^{-3}$	N_{19}	0.0071648329297	N_{31}	0.0014870043284
N_8	0.48360724197	N_{20}	$0.12577853784\cdot10^{-3}$	N_{32}	$3.151226153\cdot10^{-9}$
N_9	85.195473835	N_{21}	0.0096	N_{33}	$0.2167077474\cdot10^{-5}$
N_{10}	16607.434721	N_{22}	22240.102466	N_{34}	$0.2400055107\cdot10^{-4}$
N_{11}	$0.37521074532\cdot10^{-4}$	N_{23}	$1.4800512328\cdot10^{6}$		
N_{12}	0.028616309259	N_{24}	50.498054887		

With the viscosity and density of CH_4 defined, the viscosity of any mixture, η_m, can be calculated from the corresponding states principle

$$\eta_m = \left(\frac{T_c}{T_{c,CH_4}}\right)^{\frac{-1}{6}}\left(\frac{P_c}{P_{c,CH_4}}\right)^{2/3}\left(\frac{M_m}{M_{CH_4}}\right)^{1/2}\left(\frac{\alpha}{\alpha_{CH_4}}\right)\eta_{CH_4,P_0,T_0} \tag{6-197}$$

where CH_4 viscosity $\rho_{CH4,P0,T0}$ is calculated at temperature, T_0 and pressure P_0

$$T_0 = \left(\frac{T_{c,CH_4}}{Tc}\right) T \left(\frac{\alpha_{CH_4}}{\alpha}\right) \tag{6-198}$$

$$P_0 = \left(\frac{P_{c,CH_4}}{Pc}\right) P \left(\frac{\alpha_{CH_4}}{\alpha}\right) \tag{6-199}$$

The following mixing rules are used for the critical properties, see Ref. 48:

$$T_c = \frac{\sum_i \sum_j x_i x_j \beta_{i,j} \sqrt{T_{c,i} T_{c,j}}}{\sum_i \sum_j x_i x_j \beta_{i,j}} \tag{6-200}$$

$$P_c = \frac{8 \sum_i \sum_j x_i x_j \beta_{i,j} \sqrt{T_{c,i} T_{c,j}}}{\left(\sum_i \sum_j x_i x_j \beta_{i,j}\right)^2} \tag{6-201}$$

$$\beta_{i,j} = \left(\left(\frac{T_{c,i}}{P_{c,i}}\right)^{1/3} + \left(\frac{T_{c,j}}{P_{c,j}}\right)^{1/3}\right)^3 \tag{6-202}$$

The parameter α is

$$\alpha = 1 + 7.378 \times 10^{-3} \rho_r^{1.847} M_m^{0.5173} \tag{6-203}$$

$$\rho_r = \frac{\rho_{CH_4, \bar{P}_0, \bar{T}_0}}{\rho_{c,CH_4}} \tag{6-204}$$

where

$$\bar{T}_0 = \left(\frac{T_{c,CH_4}}{Tc}\right) T \tag{6-205}$$

$$\bar{P}_0 = \left(\frac{P_{c,CH_4}}{Pc}\right) P \tag{6-206}$$

with $\rho_{c,CH4} = 0.16284$ g/cm^3. For CH_4

$$\alpha_{CH_4} = 1 + 7.378 \times 10^{-3} \rho_r^{1.847} M_{CH_4}^{0.5173} \tag{6-207}$$

where Equation 6-204 is used. The mixture molecular weight is a function of the weight-averaged molecular weight and the number-averaged molecular weight

$$M_m = 1.304\times10^{-4}(M_W^{2.303} - M_N^{2.303}) + M_N \tag{6-208}$$

$$M_W = \frac{\sum_i x_i M_i^2}{M_N} \tag{6-209}$$

$$M_N = \sum_i x_i M_i \tag{6-210}$$

where the power in Equation 6-208 is determined by fitting to experimental viscosity data.

Note that pure species vapor viscosity correlations $\eta_{i,v}$ are not required. However, for each species i, molecular weight M_i, critical temperature, $T_{c,i}$ and critical pressure, $P_{c,i}$ must be specified.

Water (IAPWS)

The International Association of the Properties of Water and Steam recommend an equation Ref. 49- Ref. 50 for industrial application which is valid in the following range:

$$273.16\text{K} \le T \le 1173.15\text{K} \qquad 0 \le p \le p_t \tag{6-211}$$

$$T_m(p) \le T \le 1173.15\ \text{K} \qquad p_t \le p \le 300\ \text{MPa} \tag{6-212}$$

$$T_m(p) \le T \le 873.15\ \text{K} \qquad 300\ \text{MPa} \le p \le 350\ \text{MPa} \tag{6-213}$$

$$T_m(p) \le T \le 433.15\ \text{K} \qquad 350\ \text{MPa} \le p \le 500\ \text{MPa} \tag{6-214}$$

$$T_m(p) \le T \le 373.15\ \text{K} \qquad 500\ \text{MPa} \le p \le 1000\ \text{MPa} \tag{6-215}$$

where T_m is the pressure dependent melting temperature and p_t is the triple-point pressure. In accordance with industrial application recommendations, critical region correction is not applied.

Liquid

The following mixture models are available for liquid viscosity.

Molar Logarithmic Mixing

The values of pure species log liquid viscosity, $\ln \eta_{i,l}$ are mixed ideally using mole fractions x_i

$$\ln \eta_{l,m} = \sum_i x_i \ln \eta_{i,l} \tag{6-216}$$

where $\eta_{m,l}$ is the mixture viscosity of liquids.

Mass Logarithmic Mixing

The values of pure species log liquid viscosity correlation are mixed ideally using the weight fractions ω_i

$$\ln \eta_{l,m} = \sum_i \omega_i \ln \eta_{i,l} \tag{6-217}$$

Pedersen Corresponding States Model

The Pedersen Corresponding States Model described above for the gas phase viscosity also applies to the liquid phase. Pure species liquid viscosity correlations are not required. However, for each species i, molecular weight M_i, critical temperature $T_{c,i}$, and critical pressure $P_{c,i}$, must be specified.

Cubic mixing

The mixture viscosity is defined using the cubic root average in terms of the mole fractions x_i

$$\eta_{l,m} = \left(\sum_i x_i \eta_{i,l}^{1/3} \right)^3 \tag{6-218}$$

The model is noted in Ref. 51 to provide reasonable results for hydrocarbon mixtures of similar components.

The model requires that the log liquid viscosity correlation is available for all species i.

Cubic mass mixing

The mass fraction equivalent of the previous model is

$$\eta_{l,m} = \left(\sum_i \omega_i \eta_{i,l}^{1/3} \right)^3 \tag{6-219}$$

The model requires that the log liquid viscosity correlation is available for all species i.

Water (IAPWS)

The International Association of the Properties of Water and Steam recommend an equation Ref. 49- Ref. 50 for industrial application which is valid in the following range:

$$273.16\text{K} \le T \le 1173.15\text{K} \qquad 0 \le p \le p_t \tag{6-220}$$

$$T_m(p) \le T \le 1173.15\ \text{K} \qquad p_t \le p \le 300\ \text{MPa} \tag{6-221}$$

$$T_m(p) \le T \le 873.15\ \text{K} \qquad 300\ \text{MPa} \le p \le 350\ \text{MPa} \tag{6-222}$$

$$T_m(p) \le T \le 433.15\ \text{K} \qquad 350\ \text{MPa} \le p \le 500\ \text{MPa} \tag{6-223}$$

$$T_m(p) \le T \le 373.15\ \text{K} \qquad 500\ \text{MPa} \le p \le 1000\ \text{MPa} \tag{6-224}$$

where T_m is the pressure dependent melting temperature and p_t is the triple-point pressure. In accordance with industrial application recommendations, critical region correction is not applied.

DIFFUSIVITY

Two types of diffusion coefficients are supported. Diffusion coefficients in infinitely diluted systems, and Maxwell-Stefan diffusion coefficients.

For dilute systems, the binary diffusion coefficient $D^0_{i,j}$ represent the diffusivity of species i in a medium consisting of pure species j. This corresponds to the Fickian diffusion coefficient.

For any mixture, the binary Maxwell-Stefan diffusion coefficient $Đ_{i,j}$, represents the inverse drag coefficient of species i moving past species j (Ref. 55 - Ref. 58). This property is referred to as the Maxwell-Stefan diffusivity. The Maxwell-Stefan diffusivity is symmetric, $Đ_{i,j} = Đ_{j,i}$, and the diagonal elements $Đ_{i,i}$ are not used. T

Gas Phase Diffusion Coefficient at Infinite Dilution

The following models are available for the diffusion coefficients at infinite dilution in the vapor phase:

- Fuller Schettler Giddings
- Wilke-Lee

Automatic When the Gas diffusivity property model is set to Automatic, the Fuller Schettler Giddings model is used, provided that the Fuller diffusion volume is known for both species (i and j), otherwise the Wilke-Lee model is used.

Fuller Schettler Giddings

Fuller et al. (Ref. 59) modified the Chapman-Enskog relation to correlate binary diffusion coefficient for species i and j in the vapor phase according to the Fuller Schettler Giddings (FGS) model:

$$D_{i,j}^{0} = \frac{1.01325 \times 10^{-2} T^{1.75} \sqrt{\frac{1}{M_i} + \frac{1}{M_j}}}{P\left(\left(\sum_i v\right)^{\frac{1}{3}} + \left(\sum_j v\right)^{\frac{1}{3}}\right)^2} \tag{6-225}$$

where T denotes the temperature (K), M_i the molecular weight of species i (g/mol) and P is the pressure (Pa). v_i are the atomic diffusion volumes (Fuller diffusion volume), (cm^3), which are estimated using group contribution for each species (Ref. 60):

TABLE 6-7: ATOMIC AND STRUCTURAL DIFFUSION VOLUME INCREMENTS

GROUP	CONTRIBUTION
C	15.9
H	2.31
O	6.11
N	4.54
F	14.7
Cl	21
Br	21.9
I	29.8
S	22.9
Aromatic Ring	-18.3
Heterocyclic Ring	-18.3

For some simple molecules the below values, determined from regression, are used:

TABLE 6-8: DIFFUSION VOLUMES OF ATOM AND SIMPLE MOLECULES

SPECIES	FULLER DIFFUSION VOLUME
He	2.67
Ne	5.98
Ar	16.2
Kr	24.5
Xe	32.7
H_2	6.12
D_2	6.84
N_2	18.5
O_2	16.3
CO	18
CO_2	26.9
N_2O	35.9
NH_3	20.7
H_2O	13.1
SF_6	71.3
Cl_2	38.4
Br_2	69
SO_2	41.8
Air	19.7

Wilke-Lee

Wilke and Lee (Ref. 61) also modified the Chapman-Enskog relation to correlate binary diffusion coefficient in vapor phase according to:

$$D_{i,j}^{0} = 10^{-2} \times \frac{3.03 - \left(\frac{0.98}{\sqrt{MW_{i,j}}}\right) T^{1.5}}{P\sigma_{i,j}^{2}\Omega_{D}\sqrt{MW_{i,j}}} \tag{6-226}$$

where

$$MW_{i,j} = \frac{2}{\frac{1}{M_i} + \frac{1}{M_j}} \tag{6-227}$$

The length scale $\sigma_{i,j}$ for the interaction is taken from the Lennard-Jones diameter parameters of species i and j:

$$\sigma_{i,j} = \frac{(\sigma_i^{LJ} + \sigma_j^{LJ})}{2} \tag{6-228}$$

If σ_i^{LJ} is not specified in the database, it is instead estimated from:

$$\sigma_i^{LJ} = 1.18 \times 10^{-8} V_{i,l,b}^{\frac{1}{3}} \tag{6-229}$$

where $V_{i,l,b}$ is the molar volume of species at normal boiling point.

The collision integral Ω_D is evaluated from (Ref. 62):

$$\Omega_D = 1.06036\ T^{*-0.15610} + 0.19300 \exp(-0.47635\ T^*) + 1.03587 \exp(-1.52996\ T^*) + 1.76474 \exp(-3.89411\ T^*) \tag{6-230}$$

with

$$T^* = \frac{T}{\varepsilon_{i,j}} \tag{6-231}$$

The energy scale $\varepsilon_{i,j}$ for the interaction is taken from the Lennard-Jones energy parameters of species i and j:

$$\varepsilon_{i,j} = \sqrt{\varepsilon_i^{LJ} \varepsilon_j^{LJ}} \tag{6-232}$$

If ε_i^{LJ} is not specified in the database, it is instead estimated from:

$$\frac{\varepsilon_i^{LJ}}{k} = 1.15 T_{i,l,b} \tag{6-233}$$

where k is the Boltzmann constant, and $T_{i,l,b}$ is normal boiling point temperature.

Gas Phase Maxwell-Stefan Diffusivity

For gas phase diffusion the Maxwell-Stefan diffusivities are defined from the models for gas phase diffusivity at infinite dilution

$$\mathcal{D}_{i,j} = D^0_{i,j} \qquad (i \neq j) \tag{6-234}$$

All models for gas phase diffusion at infinite dilution are symmetric, the diffusivity of species i in species j equals that of species j in species i. In addition, under the ideal gas assumption, the Maxwell-Stefan diffusion coefficient matches the Fick diffusion coefficient. This implies that the Maxwell-Stefan gas diffusivities provided are independent of composition.

Liquid Phase Diffusion Coefficients at Infinite Dilution

The following models are available for the diffusion coefficients at infinite dilution in liquid phase:

- Wilke-Chang
- Tyn-Calus
- Hayduk-Minhas
- Siddiqi-Lucas
- Erkey-Rodden-Akgerman

Automatic When the Liquid diffusivity at infinite dilution property model is set to Automatic, a selection for each solute i in solvent j will be made from the models according to the following rules. Except in the case of a temperature correlation and the Erkey-Rodden-Akgerman model, all of these rules require that the log liquid viscosity correlation, $\ln \eta_j$ is available in the database for species j and that the liquid volume at normal boiling point, $V_{i,\mathrm{l,b}}$ is available for the species i.

- If a temperature correlation is available for species i and j, it is used.
- If the solvent is water, the Siddiqi-Lucas correlation (for aqueous systems) is used.
- If the solute and solvent are both normal paraffins, the Hayduk-Minhas correlation (for normal paraffins) is used.
- If the solvent is a normal paraffin, and the liquid density correlation for the solvent is available, and the solute is hydrogen, carbon-monoxide or carbon-dioxide, the Erkey-Rodden-Akgerman correlation (for normal paraffins) is used.
- If parachors P_i and P_j are both available, and the liquid volume at normal boiling point, $V_{i,\mathrm{l,b}}$ is available for the solvent, the Tyn-Calus correlation is used.
- If parachors P_i and P_j are both available, the Hayduk-Minhas correlation is used.
- If the solute and solvent are both organic molecules and the liquid volume at normal boiling point, $V_{i,\mathrm{l,b}}$ is available for the solvent, the Siddiqi-Lucas method is used.

- If the molecular weight M_j is available for the solvent, the Wilke-Chang correlation is used.
- If the solvent is a normal paraffin, and the liquid density correlation for the solvent is available, and the solute is a normal paraffin, the Erkey-Rodden-Akgerman correlation (for normal paraffins) is used.
- If the solvent is a normal paraffin, and the liquid density correlation for the solvent is available, and the Lennard-Jones diameter for the solute is available, the Erkey-Rodden-Akgerman correlation (for normal paraffins) is used.

For the Siddiqi-Lucas method, a molecule is considered organic if it has at least one C atom bound to anything else than O or C atoms. This is determined by the SMILES formula, if available. If, for any pair of species, the required input data for none of the above models is available, the entire property liquid diffusion coefficient at infinite dilution is not available.

Wilke-Chang

The correlation by Wilke and Chang (Ref. 63) for liquid phase diffusion coefficients at infinite dilution is:

$$D^0_{i,j} = 1.858795959 \times 10^{-18} \frac{T\sqrt{\phi_j M_j}}{\eta_j V^{0.6}_{i,l,b}} \tag{6-235}$$

Molecular weight, M_j and log liquid viscosity correlation, $\ln \eta_j$, for species j and liquid molar volume at normal boiling point for species i, $V_{i,l,b}$, is required. The Wilke-Chang association parameter ϕ_j, if unavailable, is set to:

TABLE 6-9: ASSOCIATION PARAMETERS FOR SOLVENT

SOLVENT	ASSOCIATION PARAMETER
Water	2.26 (Ref. 64)
Methanol	1.9
Ethanol	1.5
Others	1

Species are identified by their CAS number or SMILES formula. The Wilke-Chang correlation is not suitable for diffusion of water. If water is the solute, the correction suggested by Kooijman (Ref. 65) is applied where liquid molar volume of water at normal boiling point, $V_{water,l,b}$ is multiplied by 4.5.

Tyn-Calus

The Correlation by Tyn and Calus (Ref. 66) for liquid diffusion coefficients at infinite dilution reads:

$$D_{i,j}^{0} = 8.93 \times 10^{-16} \frac{T\left(V_{i,l,b}^{\frac{1}{6}}\right) P_j^{0.6}}{\eta_j \left(V_{j,l,b}^{\frac{1}{3}}\right) P_i^{0.6}} \tag{6-236}$$

The log liquid viscosity correlation $\ln \eta_j$ should be available for species j, The liquid volume at normal boiling point, $V_{i,l,b}$ and parachor, P_i should be available for both species i and j.

If the solvent is nonpolar (dipole moment is zero), and the solvent is methanol, ethanol or1-butanol or if the solvent is a mono-hydroxy alcohol, both the liquid volume at normal boiling point, $V_{j,l,b}$ and the parachor, P_j are corrected by a factor of $8 \times 10^3 \eta_j$.

If the solute is water, both the liquid volume at normal boiling point, $V_{i,l,b}$ and parachor, P_i for the solute are corrected by a factor 2. This factor also applies if it is detected from the SMILE formula that the species is an organic acid (a carboxyl group is found), except in the cases where the solvent is water, methanol or n-butanol.

Hayduk-Minhas

Hayduk and Minhas (Ref. 67) suggested three different correlations for liquid diffusion coefficients at infinite dilution.

Aqueous Solutions: in case the solvent is water (derived from CAS number or SMILES formula), the correlation reads:

$$D_{i,j}^{0} = 1.25 \times 10^{-12} T^{1.52} \left(\frac{0.07244359601}{V_{i,l,b}^{0.19}} - 0.292 \right) \times (\eta_j \times 10^3)^{\left(\frac{9.58 \times 10^{-6}}{V_{i,l,b}} - 1.12\right)} \tag{6-237}$$

Normal paraffin solutions: In case both the solute and solvent are normal paraffins (derived from SMILES formula), the correlation reads:

$$D^0_{i,j} = 7.30889362 \times 10^{-16} T^{1.47} \left(\frac{(\eta_j \times 10^3)^{\left(\frac{10.2 \times 10^{-6}}{V_{i,l,b}} - 0.791\right)}}{V^{0.71}_{i,l,b}} \right) \quad (6\text{-}238)$$

For all other systems, the correlation is:

$$D^0_{i,j} = 3.8934239 \times 10^{-16} \frac{T^{1.29} \sqrt{P_j}}{\eta_j^{0.92} (V^{0.23}_{j,l,b}) P_i^{0.42}} \quad (6\text{-}239)$$

If the solvent is nonpolar (dipole moment is zero), and the solvent is methanol, ethanol or1-butanol or if the solvent is a mono-hydroxy alcohol, both the liquid volume at normal boiling point, $V_{j,l,b}$ and the parachor, P_j are corrected by a factor of $8 \times 10^3 \eta_j$.

If the solute is water, both the liquid volume at normal boiling point, $V_{i,l,b}$ and parachor, P_i for solute are corrected by a factor 2. This factor also applies if it is detected from the SMILES formula that the species is an organic acid (a carboxyl group is found), except in the cases where the solvent is water, methanol or n-butanol.

Siddiqi-Lucas

Siddiqi and Lucas (Ref. 68) suggested correlations for liquid diffusion coefficients at infinite dilution for aqueous system (including gases) and for organic solutions. For normal paraffins systems, they recommended the Hayduk-Minhas model.

For aqueous solutions:

$$D^0_{i,j} = 1.295436901 \times 10^{-17} \frac{T}{\eta_j^{1.026} (V^{0.5473}_{i,l,b})} \quad (6\text{-}240)$$

For all other systems, the equation for organic solution is used as:

$$D^0_{i,j} = 1.459473761 \times 10^{-15} \frac{T(V^{0.265}_{j,l,b})}{\eta_j^{0.907} (V^{0.45}_{i,l,b})} \quad (6\text{-}241)$$

Where T is temperature, $V_{i,l,b}$ is liquid volume at normal boiling point and η_j is the viscosity of the solvent.

Erkey-Rodden-Akgerman

The correlation by Erkey et al. (Ref. 69) for liquid diffusion coefficients at infinite dilution in normal paraffins is:

$$D_{i,j}^{0} = 94.5 \times 10^{-9} \frac{\sqrt{T}(V - V_j^{ref}) \times 10^{6}}{M_i^{0.239} M_j^{0.781} (\sigma_i \sigma_j \times 10^{-20})^{1.134}} \tag{6-242}$$

where the reference volume is

$$V_j^{ref} = \frac{1}{\sqrt{2}} b_j N_{Av} \sigma_j^3 \tag{6-243}$$

N_{Av} is Avogadro's number, and the deviation from closest packing volume is given by

$$b_j = 1.206 + 0.0632 \left(\frac{\sigma_i}{\sigma_j}\right) \tag{6-244}$$

The correlation is fitted to normal paraffins, hydrogen, carbon monoxide and carbon dioxide diffusing in normal paraffins. The molecular weight M_i should be available for both solute and solvent. The Lennard-Jones diameter, σ_i is estimated from Bondi group contribution method (Ref. 70), and for some species are taken from Ref. 69 and Ref. 71 as:

TABLE 6-10: MOLECULAR DIAMETERS FOR SPECIES

SPECIES	$\sigma \times 10^{10}$ (M)
H_2	2.92
CO	3.72
CO_2	3.97
n-C_jH_{2j+2}	$(21.82+32.44*j)^{1/3}$

To prevent the diffusion coefficients from becoming negative, the minimum difference of $(V - V_j^{\text{ref}})$ is considered to be 10^{-12} mol/m^3.

Liquid Phase Maxwell-Stefan Diffusivity

The Maxwell-Stefan liquid diffusion coefficients are calculated from the liquid diffusion coefficients at infinite dilution. The diagonal values should be ignored and are set to zero. The Vignes (Ref. 72) model for diffusion in binary solutions can be extended to multi-component systems (Ref. 73):

$$Đ_{i,j} = \prod_{k=1}^{n} (Đ_{i,j,x_k \to 1})^{x_k} \tag{6-245}$$

where $Đ_{i,j,x_k \to 1}$ denotes the Maxwell-Stefan liquid diffusion coefficient for species i and j in the limited of pure species k. If k=j, it represents a binary system of species i and j where i is infinitely diluted. In addition, at infinite dilution the thermodynamics factor (activity) (Ref. 58) becomes unity and the Maxwell-Stefan diffusivity equals to Fick diffusivity:

$$Đ_{i,j,x_j \to 1} = Đ^0_{i,j} = D^0_{i,j} \tag{6-246}$$

Similarly,

$$Đ_{i,j,x_i \to 1} = Đ^0_{j,i} = D^0_{j,i} \tag{6-247}$$

Models for the $Đ_{i,j,x_k \to 1}$ for $k \neq i$ and $k \neq j$ remain to be defined in such a way that symmetry is ensured:

$$Đ_{i,j} = Đ_{j,i} \tag{6-248}$$

and to ensure continuity if both species i and j vanish:

$$\lim_{x_i \to 0} Đ_{i,j,x_k \to 1} = \lim_{x_j \to 0} Đ_{i,j,x_k \to 1} \tag{6-249}$$

For binary systems, Equation 6-245 reduces to the Vignes interpolation formula.

Wesseling-Krishna

Wesseling and Krishna (Ref. 73) proposed:

$$Đ_{i,j,x_k \to 1} = \sqrt{D^0_{i,j} D^0_{j,i}} \tag{6-250}$$

leading to:

$$Đ_{i,j} = (D^0_{i,j})^{(1+x_j-x_i)/2} (D^0_{j,i})^{(1+x_i-x_j)/2} \tag{6-251}$$

Kooijman-Taylor

Kooijman and Taylor (Ref. 74) found on a limited number of systems that this provides better results:

$$Đ_{i,j,x_k \to 1} = \sqrt{D^0_{i,k} D^0_{j,k}} \qquad (k \neq i,j) \tag{6-252}$$

leading to:

$$Đ_{i,j} = (D^0_{i,j})^{x_j}(D^0_{j,i})^{x_i}\prod_{\substack{k=1\\k\neq i,j}}^{n}(\sqrt{D^0_{i,k}D^0_{j,k}})^{x_k} \tag{6-253}$$

Wesselingh and Bollen (Ref. 75) asserted that this is a reasonable estimate.

Krishna-van Baten

Krishna and van Baten (Ref. 76), on the basis of data obtained from molecular dynamic simulations, proposed the following Vignes-based (Ref. 72) interpolation:

$$Đ_{i,j,x_k\to 1} = (D^0_{i,k})^{\left(\frac{x_i}{x_i+x_j}\right)}(D^0_{j,k})^{\left(\frac{x_j}{x_i+x_j}\right)} \qquad (k\neq i,j) \tag{6-254}$$

The model reduces to the Kooijman-Taylor model for $x_i = x_j$. The value of $Đ_{i,j,x_k\to 1}$ is undefined in the limit of both $x_i \to 0$ and $x_j \to 0$. From a physical point of view this is inconsequential as the value cancels out in the expressions obtained for the fluxes using the Maxwell-Stefan equations. Nevertheless, in order to obtain well-defined values and composition derivatives of $Đ_{i,j,x_k\to 1}$ itself, the equation is modified to:

$$Đ_{i,j,x_k\to 1} = (D^0_{i,k})^{\left(\frac{x_i+\varepsilon_x}{x_i+x_j+2\varepsilon_x}\right)}(D^0_{j,k})^{\left(\frac{x_j+\varepsilon_x}{x_i+x_j+2\varepsilon_x}\right)} \qquad (k\neq i,j) \tag{6-255}$$

where $\varepsilon_x = 10^{-10}$ is taken as a small composition. The limiting case for both $x_i \to 0$ and $x_j \to 0$ also reduces to the Kooijman-Taylor model. This equation leads to:

$$Đ_{i,j} = (D^0_{i,j})^{x_j}(D^0_{j,i})^{x_i}\prod_{\substack{k=1\\k\neq i,j}}^{n}\left((D^0_{i,k})^{\left(\frac{x_i+\varepsilon_x}{x_i+x_j+2\varepsilon_x}\right)}(D^0_{j,k})^{\left(\frac{x_j+\varepsilon_x}{x_i+x_j+2\varepsilon_x}\right)}\right)^{x_k} \tag{6-256}$$

Surface Tension

Below the available surface tension models are presented.

GAS-LIQUID SURFACE TENSION

Ideal

The gas-liquid surface tension is predicted by ideally mixing the pure species correlations. It is independent of pressure, vapor temperature or composition.

$$\sigma_{vl} = \sum_i x_{i,l}\sigma_{i,vl} \tag{6-257}$$

where the vapor-liquid surface tension correlations, $\sigma_{i,vl}$, must be specified for all species i, and are evaluated at the temperature of the liquid phase.

Winterfeld

Following Winterfeld (Ref. 77), the vapor-liquid surface tension is predicted by mixing the pure species correlations according to

$$\sigma_{vl} = \frac{\sum_i \sum_j \frac{x_{i,l}x_{j,l}\sqrt{\sigma_{i,vl}\sigma_{j,vl}}}{\rho_{i,l}\rho_{j,l}}}{\left(\sum_i \frac{x_{i,l}}{\rho_{i,l}}\right)^2} \tag{6-258}$$

It is independent of pressure, vapor temperature and composition. The vapor-liquid surface tension correlations and liquid density correlations must be specified for all species i, and are evaluated at the temperature of the liquid phase.

References

3. A. Akerberg, *CFD analyses of the gas flow inside the vessel of a hot isostatic press*, Master of Science Thesis, KTH School of Industrial Engineering and Management, Stockholm, Sweden, 2012.

4. M.A. Trebble and P.R. Bishnoi, "Accuracy and consistency comparisons of ten cubic equations of state for polar and non-polar compounds", *Fluid Phase Equilibria*, vol. 29, pp. 465–474, 1986.

5. B.E. Poling, J.M. Prausnitz, and J.P. O'Connell, *The Properties of Gases and Liquids*, McGraw-Hill, international edition, 2007.

6. M.C. Clapeyron, "Mémoire sur la puissance motrice de la chaleur," *Journal de l'École polytechnique*, vol. 23, pp. 153–190, 1834 (in French).

7. D.Y. Peng and D. Robinson, "A new two-constant equation of state," *Industrial and Engineering Chemistry: Fundamentals*, vol. 15, pp. 59–64, 1976.

8. C.H. Twu, J.E. Coon, and J.R. Cunningham, "A new generalized alpha function for a cubic equation of state, Part 1, Peng-Robinson equation," *Fluid Phase Equilibria*, vol. 105, pp. 49–59, 1995.

9. O. Redlich and J.N.S. Kwong, "On the thermodynamics of solutions an equation of state, fugacities of gaseous solutions," *Chemical Reviews*, vol. 44, no. 1, pp. 233–244, 1949.

10. G. Soave, "Equilibrium constants from a modified Redlich-Kwong equation of state," *Chemical Engineering Science*, vol. 27, no. 6, pp. 1197–1203, 1972.

11. M.S. Graboski and T.E. Daubert, "A modified Soave equation of state for phase equilibrium calculations, 3, systems containing hydrogen," *Industrial & Engineering Chemistry Process Design and Development*, vol. 18, no. 2, pp. 300–306, 1979.

12. J. R. Cooper, "Revised Release on the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam", *The International Association for the Properties of Water and Steam*, IAPWS R7-97, 2012.

13. K. Watanabe, "Revised Supplementary Release on Backward Equations for the Functions T(p,h), v(p,h) and T(p,s), v(p,s) for Region 3 of the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam", *The International Association for the Properties of Water and Steam,* Kyoto, Japan, Sep. 2004.

14. F. Marsik, "Supplementary Release on Backward Equations for Specific Volume as a Function of Pressure and Temperature v(p,T) for Region 3 of the IAPWS Industrial Formulation 1997 for the Thermodynamics Properties of Water and Steam", *The International Association for the Properties of Water and Steam,* Santorini, Greece, July 2005.

15. K.C. Chao and J.D. Seader, "A general correlation of vapor-liquid equilibria in hydrocarbon mixtures," *AIChE Journal*, vol. 7, no. 4, pp. 598–605, 1961.

16. J.H. Hildebrand and R.L. Scott, "The solubility of non-electrolytes," *Journal of Physical Chemistry*, vol. 55, no. 4, pp. 619–620, 1951.

17. H.G. Grayson and C.W. Streed, "Vapor-liquid equilibria for high temperature, high pressure hydrogen-hydrocarbon systems," *6th World Petroleum Congress*, 19–26 June, Frankfurt am Main, Germany, IV, pp. 169–180, 1963.

18. J.H. Hildebrand, J.M. Prausnitz, and R.L. Scott. *Regular and Related Solutions*, Van Nostrand Reinhold Co., 1970.

19. G.M. Wilson, "Vapor-liquid equilibrium. xi. a new expression for the excess free energy of mixing," *Journal of the American Chemical Society*, 86:127–130, 1964.

20. H. Renon and J.M. Prausnitz, "Local compositions in thermodynamic excess functions for liquid mixtures," *AIChE Journal*, vol. 14, no. 1, pp. 135–144, 1968.

21. D.S. Abrams and J.M. Prausnitz, "Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems," *AIChE Journal*, vol. 21, no. 1, pp. 116–128, 1975.

22. A. Fredenslund, R.L. Jones, and J.M. Prausnitz, "Group-contribution estimation of activity coefficients in nonideal liquid mixtures," *AIChE Journal*, vol. 21, no. 6, pp. 1086–1099, 1975.

23. S. Skjold-Joergensen, B. Kolbe, J. Gmehling, and P. Rasmussen, "Vapor-liquid equilibria by unifac group contribution. revision and extension," *Industrial & Engineering Chemistry Process Design and Development*, vol. 18, no. 4, pp. 714–722, 1979.

24. J. Gmehling, P. Rasmussen, and A. Fredenslund, "Vapor-liquid equilibria by unifac group contribution. revision and extension. 2," *Industrial & Engineering Chemistry Process Design and Development,* vol. 21, no. 1, pp. 118–127, 1982.

25. E.A. Macedo, U. Weidlich, J. Gmehling, and P. Rasmussen, "Vapor-liquid equilibria by unifac groupcontribution. revision and extension. 3," *Industrial & Engineering Chemistry Process Design and Development*, vol. 22, no. 4, pp. 676–678, 1983.

26. D. Tiegs, J. Gmehling, P. Rasmussen P, and A. Fredenslund, "Vapor-liquid equilibria by unifac group contribution. 4. revision and extension," *Industrial & Engineering Chemistry Process Design and Development*, vol. 26, no. 1, pp. 159–161, 1987.

27. H.K. Hansen, P. Rasmussen, A. Fredenslund, M. Schiller, and J. Gmehling, "Vapor-liquid equilibria by unifac group-contribution. 5. revision and extension," *Industrial & Engineering Chemistry Process Design and Development*, vol. 30, no. 10, pp. 2352–2355, 1991.

28. R. Wittig, J. Lohmann, and J. Gmehling, "Vapor-liquid equilibria by unifac group contribution. 6. revision and extension," *Industrial & Engineering Chemistry Process Design and Development*, vol. 42, no. 1, pp. 183–188, 2003.

29. K. Balslev and J. Abildskov, "Unifac parameters for four new groups," *Industrial & Engineering Chemistry Research*, vol. 41, pp. 2047–2057, 2002.

30. R.W. Hankinson and G.H. Thomson, "A new correlation for saturated densities of liquid and their mixtures," *AIChE Journal,* vol. 25, no. 4, pp. 653–663, 1979.

31. H.G. Rackett, "Equation of state for saturated liquids," *Journal of Chemical and Engineering Data*, vol. 15, no. 4, pp. 514–517, 1970.

32. L.I. Stiel and G. Thodos, "The thermal conductivity of nonpolar substances in the dense gaseous and liquid regions," *AIChE Journal*, vol. 10, no. 1, pp. 26–30, 1964.

33. M. Yorizane, S. Yoshimura, H. Masuoka, and H. Yoshida, "Thermal conductivities of binary gas mixtures at high pressures: nitrogen-oxygen, nitrogen-argon, carbon dioxide-argon, and carbon dioxide-methane," *Industrial & Engineering Chemistry Fundamentals*, vol. 22, no. 4, pp. 458–463, 1983.

34. A.L. Lindsay and L.A. Bromley, "Thermal conductivity of gas mixtures," *Industrial and Engineering Chemistry*, vol. 42, no. 8, pp. 1508–1511, 1950.

35. A. Wassiljewa, "Heat conduction in gas mixtures," *Physikalische Zeitschrift*, vol. 5, no. 22, pp. 737–742, 1904.

36. J.R. Cooper, "Release on the IAPS Formulation 1985 for the Thermal Conductivity of Ordinary Water Substance", *The International Association for the Properties of Water and Steam,* Berlin, Germany, Sep. 2008.

37. C.R. Wilke, "A viscosity equation for gas mixtures," *The Journal of Chemical Physics*, vol. 18, no. 4, pp. 517– 520, 1950.

38. R.S. Brokaw, "Approximate formulas for the viscosity and thermal conductivity of gas mixtures. ii," *The Journal of Chemical Physics*, vol. 42, no. 4), pp. 1140–1147, 1965.

39. J.E. Lennard-Jones, "On the determination of molecular fields 1. from the variation of the viscosity of a gas with temperature," *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, vol. 106, pp. 441–462, 1924.

40. W.H. Stockmayer, "Second virial coefficients of polar gases," *The Journal of Chemical Physics*, vol. 9, pp. 398–402, 1941.

41. F.M. Mourits and F.H.A. Rummens, "A critical evaluation of Lennard-Jones and Stockmayer potential parameters and of some correlation methods," *Canadian Journal of Chemical Engineering*, vol. 55, pp. 3007–3020, 1977.

42. J.A. Jossi, L.I. Stiel, and G. Thodos, "The viscosity of pure substances in the dense gaseous and liquid phases," *AIChE Journal*, vol. 8, no. 1, pp. 59–63, 1962.

43. K.S. Pedersen and P.L. Christensen, "Phase Behavior of Petroleum Reservoir Fluids," *CRC Press/Taylor & Francis Group*, 2007.

44. K.S. Pedersen, A. Fredenslund, P.L. Christensen, and P. Thomassen, "Viscosity of crude oils," *Chemical Engineering Science*, vol. 39, no. 6, pp. 1011–1016, 1984.

45. H.J.M. Hanley, W.M. Haynes, and R.D. McCarty, "The viscosity and thermal conductivity coefficients for dense gaseous and liquid methane," *Journal of Physical Chemistry*, vol. 6, no. 2, pp. 597–609, 1977.

46. K.S. Pedersen and A. Fredenslund, "An improved corresponding states model for the prediction of oil and gas viscosities and thermal conductivities," *Chemical Engineering Science*, vol. 42, no. 1, pp. 182–186, 1987.

47. R.D. McCarty, "A modified Benedict-Webb-Rubin equation of state for methane using recent experimental data," *Cryogenics*, pp. 276–280, May 1974.

48. S. Murad and K.E. Gubbins, "Corresponding states correlation for thermal conductivity of dense fluids," *Chemical Engineering Science*, 32(5):499–505, 1977.

49. J.R. Cooper, "Revised Release on the IAPWS Formulation 2008 for the Viscosity of Ordinary Water Substance", *The International Association for the Properties of Water and Steam,* Berlin, Germany, Sep. 2008.

50. K. Daucik, "Revised Release on the Pressure along the Melting and Sublimation Curves of Ordinary Water Substance", *The International Association for the Properties of Water and Steam,* Plzen, Czech Republic, Sep. 2011.

51. J. Gabitto and M. Barrufet, "Experimental and theoretical determination of heavy oil viscosity under reservoir conditions.", *Technical reports*, Office of Fossile Energy. USDOE Office of Fossil Energy, United States, 2002.

52. A. Missenard, "Conductivité thermique des liquides organiques d'une serie ou d'un 'groupe de liquides'," *Revue Générale de Thermique*, vol. 101, no. 5, pp. 649–660, 1970 (in French).

53. R.L. Rowley, G.L. White, and M. Chiu, "Ternary liquid mixture thermal conductivities," *Chemical Engineering Science*, vol. 43, no. 2, pp. 361–371, 1988.

54. R.L. Rowley, "A local composition model for multicomponent liquid mixture thermal conductivities," *Chemical Engineering Science*, vol. 37, no. 6, pp. 897–904, 1982.

55. W.D. Niven, "The Scientific Papers of James Clerk Maxwell", *Cambridge University Press*, 1890.

56. J.C. Maxwell, "On the dynamical theory of gases," *Philosophical Transactions of the Royal Society of London*, vol. 157, pp. 49–88, 1867.

57. J. Stefan, "Uber das Gleichgewicht und die Bewegung, insbesondere die Diffusion von Gasgemengen," *Sitzungsbrichte der Kaiserlichen Akademie der Wissenschaften Wien, 2te Abteilung a*, vol. 63, pp. 63–124, 1871.

58. R. Taylor and R. Krishna, "Multicomponent Mass Transfer," *Wiley-Interscience*, 1993.

59. E.N. Fuller, P.D. Schettler and J.C. Giddings, "A new method for prediction of binary gas-phase diffusion coefficients," *Industrial and Engineering Chemistry*, vol. 5, pp. 19–27, 1966.

60. E.N. Fuller, K. Ensley and J.C. Giddings, "Diffusion of halogenated hydrocarbons in helium. The effect of structure on collision cross sections," *The Journal of Physical Chemistry*, vol. 73, no. 11, pp. 3679–3685, 1969.

61. C.R. Wilke and C.Y. Lee, "Estimation of diffusion coefficients for gases and vapors," *Industrial and Engineering Chemistry*, vol. 47, no. 6, pp. 1253–1257, 1955.

62. P.D. Neufeld, A.R. Janzen and R.A. Aziz, "Empirical equations to calculate 16 of the transport collision integrals $\Omega^{(l,s)^*}$ for the Lennard-Jones (12-6) potential," *The Journal of Chemical Physics*, vol. 57, pp. 1100–1102, 1972.

63. C.R. Wilke and P. Chang, "Correlation of diffusion coefficients in dilute solutions," *AICHE Journal*, vol. 1, no. 2, pp. 264–270, 1972.

64. W. Hayduk and H. Laudie, "Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions," *AICHE Journal*, vol. 20, no. 3, pp. 611–615, 1974.

65. H.A. Kooijman, "A modification of the Stokes-Einstein equation for diffusivities in dilute binary mixture," *Industrial and Engineering Chemistry Research*, vol. 41, pp. 3326–3328, 2002.

66. M.T.Tyn and W.F Calus. Diffusion Coefficients in dilute binary mixtures. Journal of Chemical and Engineering Data, vol. 20, no. 1, pp. 106–109, 1975.

67. W.Hayduk and B.S.Minhas, "Correlation for prediction of molecular diffusivities in liquids," *Canadian Journal of Chemical Engineering*, vol. 60, no. 2), pp. 295–299, 1983.

68. M.A. Siddiqi and K. Lucas, "Correlations for prediction of diffusion in liquids", *The Canadian Journal of Chemical Engineering*, vol. 64, pp. 839–843, 1986.

69. C. Erkey, J.B. Rodden and A. Akgerman, "A correlation for predicting diffusion coefficients in alkanes", *The Canadian Journal of Chemical Engineering*, vol. 68, pp. 661–665, 1990.

70. A. Bondi, "Van der waals volumes and radii", *Journal of Physical Chemistry*, vol. 68, no. 3, pp. 441-451, 1964.

71. J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, "The Molecular Theory of Gases and Liquids", *Wiley-Interscience*, 1964.

72. A. Vignes, "Diffusion in Binary Solutions," *Industrial and Engineering Chemistry Fundamentals*, vol. 5, pp. 189–199, 1966.

73. J.A. Wesselingh and R. Krishna, "Mass Transfer", *Ellis Horwood Ltd*, 1990, ISBN: 0-13-553165-9.

74. H.A. Kooijman and R. Taylor, "Estimation of diffusion coefficients in multicomponent liquid systems", *Industrial and Engineering Chemistry Research*, vol. 30, pp. 1217–1222, 1991.

75. J.A. Wesselingh and A.M. Bollen, "Multicomponent diffusivities from the free volume theory", *Chemical Engineering Research and Design*, 75(6):590–602, 1997.

76. R. Krishna and J.M. van Baten, "The Darken relation for multicomponent diffusion in liquid mixtures of linear alkanes: An investigation using molecular dynamics (MD) simulations," *Industrial and Engineering Chemistry Research*, vol. 44, pp. 6939–6947, 2005.

77. P.H. Winterfield, L.E. Scriven, and H.T. Davis, "An approximate theory of interfacial tension of multicomponent systems: Applications binary liquid-vapor tensions," *AIChE Journal*, vol. 24, no. 6, pp. 1010–1014, 1978.

78. Selection of a thermodynamic model, Available online at http://people.clarkson.edu/~wwilcox/Design/thermodl.htm.

79. E.C. Carlson, "Don't Gamble With Physical Properties For Simulation", *Chemical Engineering Progress*, vol. 92, no. 10, pp. 35–46, 1996.

7

Glossary

This Glossary of Terms contains application-specific terms used in the Chemical Reaction Engineering Module software and documentation. For finite element modeling terms, mathematical terms, and geometry and CAD terms, see the glossary in the *COMSOL Multiphysics Reference Manual*. For references to more information about a term, see the index.

Glossary of Terms

absorption Uptake of a gas into the bulk of a liquid. Gas absorption takes place for example in the liquid of a scrubber tower where an up-streaming gas is washed by a down-going flow of a scrubber solution.

adsorption Attachment of a molecule or atom to a solid surface. Adsorption involves a chemical bond between the adsorbed species and the surface.

anisotropy Variation of a transport property in different directions in a material. Is often obtained from homogenization of regular structures, for example, monolithic structures in tubular reactors.

Arrhenius rate equation Expression that relates the rate constant of a chemical reaction to the exponential of the temperature.

batch reactor Reactor characterized by its operation, which means that the reactor does reaches steady state.

bipolar plate Electrically conducting plate connected to the anode on one side and to the cathode on the other side in an electrochemical cell.

Brinkman equations Extension of Darcy's law in order to include the transport of momentum through shear in porous media flow.

Butler-Volmer equation Expression that relates the reaction rate of an electron transfer reaction on an electrode surface to the exponential of the overpotential. The equation can be derived from the Arrhenius rate equation by accounting for the contribution of the electric potential to the activation energy.

boundary layer Region in a fluid close to a solid surface. This region is characterized by large gradients in velocity and is often treated with approximate methods because it is difficult to geometrically resolve the large gradients found there.

chemisorption See *adsorption*.

continuous reactor Reactor that operates without interruption. This type of reactor is characterized by its steady-state operation.

diffusion layer Fictitious layer in a fluid close to a solid surface where a chemical reaction takes place. The flux of species perpendicular to the surface in this layer is dominated by diffusion.

Darcy's law Equation that gives the velocity vector as proportional to the pressure gradient. Often used to describe flow in porous media.

electrokinetic flow Transport of fluid or charged particles within a fluid by means of electric fields.

electroneutrality condition Condition that states that the sum of charges in a control volume in an electrolyte should be zero.

electrophoresis Migration of charged electrolyte ions in an electric field.

electroosmosis Onset of a flow due to the application of an external electric field or due to the formation of an electric field created by ion transport in membranes, for example.

Euler flow Flow at high velocities, where incompressibility of the fluid is of importance whereas the influence of viscous momentum transport is negligible.

Fick's laws The first law relates the concentration gradients to the diffusive flux of a solute infinitely diluted in a solvent. The second law introduces the first law into a differential material balance for the solute.

fully developed laminar flow Laminar flow along a channel or pipe that only has velocity components in the main direction of the flow. The velocity profile perpendicular to the flow does not change downstream in the flow.

Hagen-Poiseuille equation See *Poiseuille's law*.

heterogeneous reaction Reaction that takes place at the interface between two phases.

homogeneous reaction Reaction that takes place in the bulk of a solution.

law of the wall See *wall function*.

Maxwell-Stefan equations Set of equations that describe the diffusion of solutes and solvent in a concentrated solution. In such a solution, the solutes interact with each other and with the solvent.

migration The transport of charged species in an electrolyte due to the electric force imposed by the electric field.

monolithic reactor Catalytic reactor made of one single piece of solid material. Incorporates a catalytic structure in its often porous structure.

Navier-Stokes equations Equations for the momentum balances coupled to the equation of continuity for a Newtonian incompressible fluid.

Nernst-Planck equation Equation that describes the flux of an ion through diffusion, convection, and migration in an electric field. The equation is valid for diluted electrolytes.

Newtonian flow Flow characterized by a constant viscosity or a viscosity that is independent of the shear rate in the fluid.

physisorption See *adsorption*.

Poiseuille's law Equation that relates the mass rate of flow in a tube as proportional to the pressure difference per unit length and to the fourth power of the tube radius. The law is valid for fully developed laminar flow.

Soret effect Mass diffusion in multicomponent mixtures due to temperature gradients.

specific surface area Internal surface area of a porous structure given in area per unit volume, which yields the unit one over unit length. Often used to characterize the structure of porous catalysts.

streamline-diffusion stabilization A numerical technique for stabilization of the numeric solution to a convection-dominated PDE by artificially adding diffusion in the direction of the streamlines.

surface molar flux the tangential flux in the surface dimension as governed by diffusion according to Fick's law.

wall function Semi-empirical expression for the anisotropic flow close to a solid surface used in turbulence models. Often based on negligible variations in pressure gradient in the direction tangential to the surface.

Index

A
AC/DC Module 123
activation energy 35
adding species 123
additional sources (node) 81
adsorption 226, 239
Application Libraries window 21
application library examples
  CHEMKIN 54
  convection and diffusion 204
  migration in electric field 204
  surface reactions 304
  transport of concentrated species 250
  transport of diluted species 199
  variables with scope 29
Arrhenius parameters 71, 105
association factor of solvents 51

B
batch reactor (constant volume) 44
batch reactors, defined 58
batch reactors, theory 43
Battery Design Module 123
boundary electrolyte potential 299
boundary nodes
  Nernst-Planck equations 278
  surface reactions 304
  transport of concentrated species 251
  transport of diluted species 200, 295
Butler-Volmer equation 283

C
CAPE-OPEN compliant packages 335
CFD Module 123
chemical equilibrium 27, 68, 102
chemical formula identification number 28
chemistry interface
  theory 34
CHEMKIN 26, 53
common settings 19
concentration (node)
  Nernst-Planck equations 282
  transport of diluted species 209
concentration of species 123
concentration variables, scaling 66
continuity equation, Nernst-Planck equations 190
convection 138
convection, diffusion, and migration (node)
  Nernst-Planck equations 279
convective terms 31
convective terms, diluted species 130
convective terms, Nernst-Planck equations 189
critical point 351
CSTR (constant volume), defined 58
CSTR (constant volume), theory 45
CSV files 93
current (node) 299
current density (node) 285, 299
current discontinuity (node) 286

D
Darcy velocity 138
defining species concentration 123
diffusion models 246
diffusivity
  gas phase, solvents 50
  liquid phase, solvents 50
dipole moment transport parameter 76, 109
documentation 20
domain nodes
  electrophoretic transport interface 295
  Nernst-Planck equations 278

transport of concentrated species 251
transport of diluted species 200
Dusty gas model 247

E edge nodes
surface reactions 304
electric insulation (node) 281
electrode-electrolyte interface coupling (node)
transport of diluted species 218, 263
electrophoretic transport interface 289
emailing COMSOL 22
enthalpy of formation 351
entropy of formation 351
Equilibrium Reaction
theory for 128
equilibrium reaction (node) 215, 273
equilibrium reaction group (node) 79, 112
equilibrium reactions 41
experiment (node) 93
external thermodynamic packages 335

F Faraday's law 135
feed inlet (node) 83
Fick equations and diffusivities 158
Fick's law approximation diffusion 164
Fick's law diffusion model 248
flash calculation
retrograde solution type 351
solution type 351–352
flash calculations 349
flux (node) 241, 301
Nernst-Planck equations 283
transport of concentrated species 269
transport of diluted species 209, 241, 301
flux discontinuity (node) 211
Nernst-Planck equations 285
transport of concentrated species 272
transport of diluted species 211
frequency factors 35
Freundlich exponent 144

G gas constant 35, 194
gas diffusion 158
gas phase solvents 52
gas reacting fluids 61, 74, 97, 108
Gibbs free energy 73, 107

H half-cell 285
Heat Transfer Module 123
Hygroscopic Swelling 233

I importing
CHEMKIN files 53
inflow (node) 208, 301
Nernst-Planck equations 284
transport of concentrated species 270
initial values (node)
Nernst-Planck equations 281
reaction engineering 66
surface reactions 306
transport of concentrated species 267
transport of diluted species 205
insulation (node) 299
internet resources 19
irreversible reaction 27, 68, 102

J junction potentials 190

K kinetic gas theory 50
knowledge base, COMSOL 22
Knudsen diffusion 247

L labeling rules, reaction nodes 29
Langmuir constant 144
Lennard-Jones potential 76, 109
line mass source (node)
species transport 213
line source
species transport 132

liquid reacting fluids 61, 74, 97, 108

M mass action law 34
mass action law, laminar flow 193
mass based concentrations (node) 205
mass fraction (node) 268
mass fractions 123
mass transport 157
Maxwell-Stefan diffusion model 247
Maxwell-Stefan diffusivity matrix 161
mixture-averaged diffusion model 162, 248
monolayer adsorption 183
MPH-files 21
multicomponent diffusion 160
multiphase flash calculations 336

N Nernst-Einstein relation 134, 203, 221, 225
Nernst-Planck equations interface 275
theory 188
Nernst-Planck-Poisson Equations interface 288
no flux (node) 207
Nernst-Planck equations 281
transport of concentrated species 271
nodes, common settings 19
nonconservative formulations 130, 190

O Ohm's law 135
open boundary (node)
Nernst-Planck equations 286
transport of concentrated species 272
transport of diluted species 214
outflow (node)
electrophoretic transport 302
Nernst-Planck equations 284
transport of concentrated species 271
transport of diluted species 208

P packed bed reactors 147
nonspherical particles 153, 172
pair nodes
electrophoretic transport interface 295
surface reactions 304
transport of concentrated species 251
transport of diluted species 200
parameter estimation, solver 116
partially saturated porous media (node) 222
periodic condition (node)
transport of diluted species 212
persistence
of thermodynamic packages 339
physics interfaces 15
physics interfaces, common settings 19
plug flow reactors 48, 58
point mass source (node)
species transport 213
point nodes
surface reactions 304
point source
species transport 131
porous electrode coupling (node) 217
porous media transport properties (node) 219, 222
potential (node) 299
predefined expressions, reaction engineering 54
pseudo time step 191

R reacting fluids, gases and liquids 61, 74, 97, 108
Reacting Volume 206, 244
reaction (node) 67, 101
reaction coefficients (node) 218
reaction engineering interface 57, 61
theory 34
reaction selection list 28

reaction terms 188
reaction thermodynamics (node) 82, 114
Reactions
in porous catalyst pellets 231
reactions (node)
Nernst-Planck equations 282
reacting flow, laminar flow 265
surface reactions 306
transport of concentrated species 266
transport of diluted species 205
Reactive pellet bed 165
reactive pellet bed 147
reactive pellet bed (node) 228, 259
reactor types
batch (constant volume) 44
batch, defined 58
batch, theory 43
CSTR (constant volume), defined 58
CSTR (constant volume), theory 45
plug flow, definition 58
plug flow, theory 48
semibatch, definition 58
semibatch, theory 47
removing species 123
retardation factor 144
reversible reaction 27, 68, 102
reversible reaction group (node) 77, 110
RF Module 123

S selecting
chemical species transport interfaces 119
space dimensions and physics interfaces 15
semibatch reactors 47, 58
solute-solvent approximations 31
solvents, association factor of 51
solver settings, parameter estimation 116
solver time, discretization and 66
Soret effect 165
space dimensions 15
species (node) 73, 107
species activity (node) 82, 114
species group (node) 80, 113
species names, syntax for 31
species source (node) 300
species thermodynamics (node) 82, 114
species types 31
standard settings 19
Stiel-Thodos equation 52
Stockmayer potential 76, 109
stoichiometric coefficients 73, 107
stratified porous media 142
superficial volume averages, porous media 138
Supporting Electrolytes 134
supporting electrolytes
theory, Nernst-Planck equations 188
surface concentration (node) 307
surface equilibrium reaction (node) 217, 274
surface properties (node) 305
surface reactions interface 303
theory 182
symmetry (node)
Nernst-Planck equations 283
transport of concentrated species 272
transport of diluted species 210

T Tafel equation 283
technical support, COMSOL 22
temperature exponents 35
theory
chemistry interface 34
Nernst-Planck equations 188
reaction engineering 34
surface reactions 182

transport of concentrated species interface 157
transport of diluted species in porous media interface 127
transport of diluted species interface 126
thermal conductivity 52
thermal diffusion 165
thermodynamics package 335
adding 336
thickness
fracture 234
thin diffusion barrier (node) 214
Thin Impermeable Barrier 215
tortuosity factors 140
transport mechanisms 252, 256, 259
transport of concentrated species interface 245
theory 157
transport of diluted species in porous media interface 199
theory 127
transport of diluted species interface 195, 236
theory 126
turbulent mixing (node)
transport of concentrated species 264
transport of diluted species 204

U uniform scaling 66

V variable scope 29

W websites, COMSOL 22
Wilke-Chang equation 50