Fuel Cell & Electrolyzer Module

User's Guide

6.2

COMSOL

Fuel Cell & Electrolyzer Module User's Guide

Version: COMSOL 6.2

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Contents

Chapter 1: Introduction

Chapter 2: Modeling with Electrochemistry

Chapter 3: Fuel Cell and Electrolyzer Interfaces

Chapter 4: Electrochemistry Interfaces

Chapter 5: Chemical Species Transport Interfaces

Chapter 6: Fluid Flow Interfaces

Chapter 7: Heat Transfer Interfaces

Chapter 8: Thermodynamics

Chapter 9: Multiphysics Coupling Nodes

Chapter 10: Glossary

1

Introduction

This guide describes the Fuel Cell & Electrolyzer Module, an optional add-on package for COMSOL Multiphysics® designed to assist you in building detailed models of the various reactions and transport processes in fuel cells and electrolyzers.

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 Fuel Cell & Electrolyzer Module
- Overview of the User's Guide

About the Fuel Cell & Electrolyzer Module

In this section:

- What Can the Fuel Cell & Electrolyzer Module Do?
- Fuel Cell & Electrolyzer Module Physics Interface Guide
- Common Physics Interface and Feature Settings and Nodes
- Where Do I Access the Documentation and Application Libraries?

What Can the Fuel Cell & Electrolyzer Module Do?

The Fuel Cell & Electrolyzer Module extends the COMSOL Multiphysics environment with customized physics interfaces for modeling of fuel cells and electrolyzers. These physics interfaces provide tools for building detailed models of the configuration of the various parts constituting electrochemical energy converters. The interfaces include descriptions of the electrochemical reactions and the transport properties that influence the performance in terms of fuel or electricity consumption, energy efficiency and cooling requirements. With this module, you have the perfect tools to investigate the influence of using different materials, geometric configurations, and operating conditions.

The core functionality of the module are the electrochemistry interfaces. Generic electrochemistry interfaces for various types (primary, secondary, and tertiary) current distributions are available, which may be used for modeling both solid nonporous as well as for porous electrodes. In addition to these generic electrochemistry interfaces, the module also contains dedicated Hydrogen Fuel Cell and Water Electrolyzer interfaces.

The tailored physics interfaces mentioned above are also complemented with extended functionality in other physics interfaces for chemical species transport, heat transfer,

and fluid flow. In particular, the fluid flow interfaces are extended to also include functionality to model two-phase flow.

	A selection of suitable materials are also available in the Fuel Cell and Electrolyzer Material Library. For more detailed information about materials, see Materials in the *COMSOL Multiphysics Reference Manual*.

Finally, the Fuel Cell & Electrolyzer Application Library includes a number of tutorials (model examples) for various types of fuel cell and electrolyzers.

See Where Do I Access the Documentation and Application Libraries? to locate and use these examples and tutorials as a starting point to your own investigations.

Fuel Cell & Electrolyzer Module Physics Interface Guide

The table lists the physics interfaces available with this module in addition to the core physics included with COMSOL Multiphysics.

	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				
Transport of Diluted Species		tds	all dimensions	stationary; time dependent
Transport of Concentrated Species		tcs	all dimensions	stationary; time dependent
Chemistry		chem	all dimensions	stationary; time dependent

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
Nernst–Planck–Poisson Equations		tds+es	all dimensions	stationary; time dependent; stationary source sweep; small-signal analysis, frequency domain
Electrophoretic Transport		el	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization
Transport of Diluted Species in Porous Media		tds	all dimensions	stationary; time dependent
Transport of Concentrated Species in Porous Media		tcs	all dimensions	stationary; time dependent
Surface Reactions		sr	all dimensions	stationary (3D, 2D, and 2D axisymmetric models only); time dependent
Transport of Diluted Species in Fractures		dsf	3D, 2D, 2D axisymmetric	stationary; time dependent
〰 **Reacting Flow**				
Laminar Flow		—	3D, 2D, 2D axisymmetric	stationary; time dependent
Laminar Flow, Diluted Species		—	3D, 2D, 2D axisymmetric	stationary; time dependent
〰 **Nonisothermal Reacting Flow**				
Laminar Flow		—	3D, 2D, 2D axisymmetric	stationary; time dependent
Reacting Flow in Porous Media				
Transport of Diluted Species		—	3D, 2D, 2D axisymmetric	stationary; time dependent
Transport of Concentrated Species		—	3D, 2D, 2D axisymmetric	stationary; time dependent

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
Electrochemistry				
Primary Current Distribution Secondary Current Distribution		cd	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent
Tertiary Current Distribution, Nernst–Planck (Electroneutrality, Water-Based with Electroneutrality, Supporting Electrolyte)		tcd	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent
Electroanalysis		tcd	all dimensions	stationary; time dependent; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent; cyclic voltammetry
Electrode, Shell		els	3D, 2D, 2D axisymmetric	stationary; time dependent
Hydrogen Fuel Cell Interfaces		fc	all dimensions	stationary; time dependent; frequency domain
Water Electrolyzer Interfaces		fc	all dimensions	stationary; time dependent; frequency domain
Fluid Flow				
Multiphase Flow				
Bubbly Flow				
Laminar Bubbly Flow		bf	3D, 2D, 2D axisymmetric	stationary; time dependent

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
Mixture Model				
Mixture Model, Laminar Flow		mm	3D, 2D, 2D axisymmetric	stationary; time dependent
Euler–Euler Model				
Euler–Euler Model, Laminar Flow		ee	3D, 2D, 2D axisymmetric	stationary; time dependent
Phase Transport Mixture Model				
Phase Transport, Mixture Model, Laminar Flow		—	3D, 2D, 2D axisymmetric	stationary; time dependent
Phase Transport				
Phase Transport		phtr	all dimensions	stationary; time dependent
Phase Transport in Porous Media		phtr	all dimensions	stationary; time dependent
Phase Transport in Free and Porous Media Flow		phtr	all dimensions	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
Multiphase Flow in Porous Media		—	all dimensions	stationary; time dependent
Multiphase Free and Porous Media Flow		—	3D, 2D, 2D axisymmetric	stationary; time dependent
Free and Porous Media Flow, Brinkman		fp	3D, 2D, 2D axisymmetric	stationary; time dependent

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
Free and Porous Media Flow, Darcy		—	3D, 2D, 2D axisymmetric	stationary; time dependent
≋ **Nonisothermal Flow**				
Brinkman Equations		—	3D, 2D, 2D axisymmetric	stationary; time dependent; stationary, one-way NITF; time dependent, one-way NITF
⦚ **Heat Transfer**				
Heat Transfer in Porous Media		ht	all dimensions	stationary; time dependent

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 online 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 on 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.

Win	To open the **Documentation** window: • Press Ctrl+F1. • From the **File** 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 **File** menu, select **Application Libraries**. To include the latest versions of model examples, from the **File>Help** menu select (▦) **Update COMSOL Application Libraries**.

(Mac) (Linux)	From the **File** or **Windows** menu, select **Application Libraries**. To include the latest versions of model examples, from the **Help** menu select (▦) **Update COMSOL Application Libraries**.

CONTACTING COMSOL BY EMAIL

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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 will be 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.

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COMSOL Access	www.comsol.com/access
Support Center	www.comsol.com/support
Product Download	www.comsol.com/product-download
Product Updates	www.comsol.com/product-update
COMSOL Blog	www.comsol.com/blogs
Discussion Forum	www.comsol.com/forum
Events	www.comsol.com/events
COMSOL Application Gallery	www.comsol.com/models
COMSOL Video Gallery	www.comsol.com/videos
Support Knowledge Base	www.comsol.com/support/knowledgebase

Overview of the User's Guide

The *Fuel Cell & Electrolyzer Module User's Guide* gets you started with modeling using COMSOL Multiphysics. The information in this guide is specific to this module. Instructions how to use COMSOL in general are included with the *COMSOL Multiphysics Reference Manual*.

> 💡 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.

TABLE OF CONTENTS, GLOSSARY, AND INDEX

To help you navigate through this guide, see the Contents, Glossary of Terms, and Index.

MODELING WITH ELECTROCHEMISTRY

The Modeling with Electrochemistry chapter discusses a variety of topics, including Fundamentals of Electrochemistry Modeling, Modeling Electrochemical Reactions, Modeling Cyclic Voltammetry, and Postprocessing Your Solution.

THE FUEL CELL AND WATER ELECTROLYZER INTERFACES

The Fuel Cell and Electrolyzer Interfaces chapter describes the Hydrogen Fuel Cell and the Water Electrolyzer interfaces.

THE ELECTROCHEMISTRY INTERFACES

The Electrochemistry Interfaces chapter describes the Primary Current Distribution; Secondary Current Distribution; Tertiary Current Distribution, Nernst–Planck; Electrode, Shell; and Electroanalysis interfaces.

THE CHEMICAL SPECIES TRANSPORT INTERFACES

The Chemical Species Transport Interfaces chapter describes the Transport of Diluted Species, Transport of Concentrated Species, the Transport of Diluted Species in Porous Media, the Surface Reaction and the Reacting Flow interfaces.

THE FLUID FLOW INTERFACES

The Fluid Flow Interfaces chapter describes, among others, the Darcy's Law and Free and Porous Media Flow interfaces, included under the Porous Media and Subsurface

Flow branch, as well as the Bubbly Flow, Mixture Model and Euler-Euler interface, included under the Multiphase Flow branch.

The Laminar Flow interface is also available and is described in the *COMSOL Multiphysics Reference Manual*.

THE HEAT TRANSFER INTERFACES

The Heat Transfer Interfaces chapter describes how electrochemical heat sources can be coupled to heat transfer, and the theory for how these are calculated.

THERMODYNAMICS

This chapter describes the functionality of the Thermodynamics node to define thermo-physical and transport properties.

THE MULTIPHYSICS COUPLING NODES

The Multiphysics Coupling Nodes chapter describes the coupling nodes available under the Multiphysics node for coupling various electrochemical interfaces using flow, potential, and temperature couplings, for example.

2

Modeling with Electrochemistry

In this chapter:

- Introduction to Electrochemistry Modeling

Introduction to Electrochemistry Modeling

In this section:

What Is Electrochemistry?

An *electrochemical* process is one that either converts electrical energy to chemical energy or converts chemical energy to electrical energy.

In electrochemical reactions, chemicals react by gaining or losing electrons. Chemicals can exchange these electrons with an electrical conductor or circuit. The chemical potential — or thermodynamic driving force — for a chemical reaction is thus converted into an electrical potential or voltage, which can be exploited to do useful work when an electrical current is drawn.

Electrochemical Applications

Electrochemical systems may be classified in different ways.

One approach is to contrast those electrochemical systems involving desirable reactions from those involving undesirable reactions. Synthetic *electrolysis* is an example of a desirable reaction because the chemical process is promoted to generate a desired product. Or, for example, when designing a battery we might want to set up conditions to promote an electrochemical reaction in order to extract useful energy.

Corrosion is an example of undesirable electrochemistry because in this case spontaneous electrochemical reactions destroy structural materials and so harm the integrity of a system: we aim to minimize the rate of these reactions.

Electrochemical systems can also be classified into systems that output energy or systems that consume energy. *Batteries and fuel cells* are energy extraction devices — an electrochemical reaction is used to convert the energy in chemical system into a voltage. Such cells are also called *galvanic cells*. By contrast, in *electrolysis*, the system consumes energy to promote an electrochemical reaction for synthesis. Similar electrochemical systems needing energy input include manufacturing processes such as *electroplating*. Electrochemical reactions may also be driven for *electroanalysis*, to quantify or otherwise explore the chemical constituents or reactivity of a system.

The different electrochemical modules in COMSOL Multiphysics are designed to offer tailored physics interfaces provision for each of these electrochemical situations. The underlying physical description provided by the general physics interfaces described below is common to all the modules — the differences between the modules lies in the particular expected system inputs and outputs and the intended behavior of the system.

Fundamentals of Electrochemistry Modeling

Electrochemical systems consist of electrically conducting media. These may be classified as electrodes or electrolytes. An *electrode* carries current by transport of electrons; normally the electrode is a conventional electrical conductor such as a metal. The *electrolyte* carries current by transport of charged chemical species (ions). Electrolytes are often salt solutions in water but may include salt solutions in other liquid solvents, as well as solids, such as concrete, which can conduct by transport of oxide ions. The electrical conductivity of an electrode is normally several orders of magnitude larger than the electrical conductivity of an electrolyte.

THE ELECTRODE-ELECTROLYTE INTERFACE

At the *electrode-electrolyte interface*, conventional electrical current in the electrode is converted into ionic current in the electrolyte. According to the overall conservation of charge, these currents must balance here. The conversion between the two types of currents may arise due to electrochemical reaction (electrolysis) or capacitive charging.

Electrolysis occurs when a chemical species in the electrolyte exchanges one or more electrons with the electrode. Capacitive charging occurs when the potential of an electrode is changing, so that ions in the electrolyte are either attracted or repelled from the surface, drawing a current.

Batteries and fuel cells can also involve porous electrodes, in which an electrode material has a micro- or nanostructure that is permeable to an electrolyte solution. The advantage of such a material is the great increase in the area of the electrode-electrolyte interface.

Note that all current must move in circuits. An isolated electrode-electrolyte interface cannot draw a net current, but a system with two such interfaces can. An electrochemical system with two or more electrodes in contact with electrolyte is called an *electrochemical cell.*

In an electrochemical cell with two electrodes, these electrodes are identified as an *anode*, at which the electrochemical reaction transfers electrons from electrolyte to electrode, and a *cathode*, at which electrons are transferred from the electrode to the electrolyte. Note that it is the direction of the current that will determine if an electrode reaction is anodic or cathodic. For a battery, for instance, the location of the anode and cathode will change depending on whether the battery is charged or discharged. (The general habit in the battery community to always denounce the positive electrode as the "cathode" is hence strictly only correct during battery discharge.)

Conventional electric current is the flow of positive charge, which is then from anode to cathode through the electrolyte. A closed circuit, conserving overall system charge, is formed by the flow of electric current in the electrode domains (and any electrical circuitry) from cathode to anode, and by the transport of ions through the electrolyte domains from anode to cathode.

OUTPUTS OF INTEREST FROM A MODEL

The experimentally measurable features of an electrochemical system are the external (lumped) current and voltage acting between the two electrodes. It is, in general, impossible to measure local current densities or potentials at different points on the

surface of a conducting electrode, or at arbitrary points within an electrochemical system.

The advantage of physical modeling is the ability to investigate the full space-dependent behavior of the system under a wide range of circumstances to identify the reasons for the observed current-voltage relationship, and so to identify the appropriate physical conditions to optimize current and voltage as required.

The overall current-voltage curve of an electrochemical cell is also known as a *polarization curve* or, in an analytical context, a *voltammogram*. These curves are not unique but rather depend on the means by which the current or voltage is altered, since these lumped parameters are related to multiple physical effects with different length and time scales. Hysteresis in practical polarization curves is not uncommon.

Polarization curves are frequently nonlinear. The combination of nonlinearity and hysteresis means that electrochemical cells do not necessarily resemble "ideal" electrical components (such as a circuit of resistors and capacitors) in the sense of giving a predictable and linear current-voltage response.

Current Distribution Cases and Choosing the Right Interface to Model an Electrochemical Cell

COMSOL Multiphysics has many built-in physics interfaces aimed at specific applications. In many generic cases, however, the modeler has to make some basic assumptions about his system before starting to build his model.

Under the assumption of a linear relation of current density to electric field, Ohm's law is obeyed for the electrolyte current. This is the assumption of *primary current distribution*, where one also assumes infinitely fast electrodes kinetics, resulting in negligible potential drops over the electrode-electrolyte interfaces. If the electrode reaction kinetics proceed at a finite rate, then the system has a *secondary current distribution*. In cases where more advanced nonlinear charge conservation equations and concentration-dependent electrode polarization are required, the system is described as obeying *tertiary current distribution*.

In some applications, especially within the field of *electroanalysis*, the potential gradients in the electrolyte are so small that the spatial distribution of current in the

electrolyte is not solved for. Such models are instead centered around the interplay of electrode kinetics and transport (by diffusion) of the reacting species in the vicinity of the electrode.

A rule-of-thumb flowchart for selecting a proper current distribution interface for a model is shown below. The recommendations here are indicative and the modeler may sometimes want to deviate from the suggested route; in particular, simpler descriptions are recommended at an earlier stage of model development. In the following sections we explain some of the theory behind this flowchart with regards to the description of the electrolyte charge transport and electrode reactions.
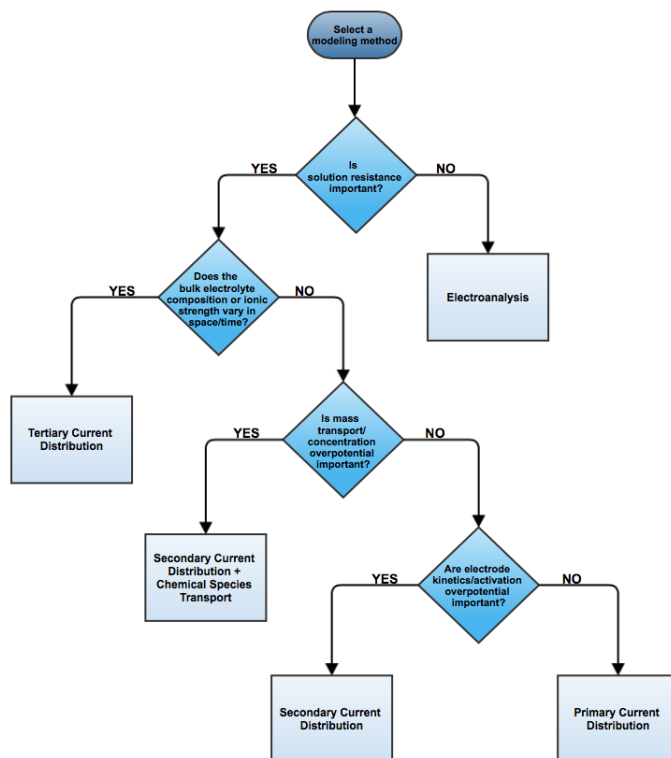
Understanding the Different Approximations for Conservation of Charge in Electrolytes

Deciding how to model the charge transport in the electrolyte is usually the starting point when setting up an electrochemical model since this will determine what physics

interface you will use when starting to build your model. Different theoretical descriptions of the electrolyte current density are included in COMSOL Multiphysics. They are applicable in different circumstances as discussed in this section.

The electric displacement field in a medium is related to the local charge density according to Gauss's law, one of Maxwell's equations:

$$\nabla \cdot \mathbf{D} = \rho_v$$

In electrolytes, we can normally assume that the electrical permittivity is constant and equal to a bulk value:

$$\mathbf{D} = \varepsilon_0 \varepsilon_s \mathbf{E} = -\varepsilon_0 \varepsilon_s \nabla V$$

Hence

$$\nabla^2 V + \frac{\rho_v}{\varepsilon_0 \varepsilon_s} = 0$$

In an electrolyte with ionic charge carriers, the charge density can be written as:

$$\rho_v = F \sum_i z_i c_i$$

Hence

$$\nabla^2 V + \frac{F}{\varepsilon_0 \varepsilon_s} \sum_i z_i c_i = 0$$

This is the *Poisson equation* relating the electrolyte potential to the distribution of charge carriers within the electrolyte. In its derivation we assumed that the only charge carriers are ions, and that the solvated ions and electric field do not alter the permittivity of the medium.

The mass transport of the charge carriers in aqueous systems is normally given by the *Nernst–Planck equations*. These equations neglect ion-ion interactions, and so they are only exact for infinitely dilute solutions:

$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_l + c_i \mathbf{u}$$

Note that concentrated electrolyte systems, such as those in many batteries, use an extended concentrated species flux definition, based on the Maxwell–Stefan set of

equations. This will result in a different set of equations to solve for, but the general principles and conclusion in this section will be the same.

Substituting the Nernst–Einstein relation for the electrical mobility of an ion we get:

$$\mathbf{N}_i = -D_i\left(\nabla c_i + \frac{z_i F}{RT}\, c_i \nabla \phi_l\right) + c_i \mathbf{u}$$

The above expressions for the n species i, together with the Poisson equation, give a set of $n+1$ equations in $n+1$ unknowns. These are the *Nernst–Planck–Poisson equations*. They can be defined in COMSOL Multiphysics by coupling **Transport of Diluted Species** with **Electrostatics**, or by using the **Tertiary Current Distribution, Nernst-Planck** interface with **Charge conservation model: Poisson**, but they are highly nonlinear and difficult to converge. Most often, further approximations can simplify the problem without compromising accuracy.

⚲
- Theory for the Transport of Diluted Species Interface
- Theory of Electrostatics in the *COMSOL Multiphysics Reference Manual*

An important dimensional quantity occurring in the Poisson equation is:

$$x_\mathrm{D} = \sqrt{\frac{RT \varepsilon_0 \varepsilon_\mathrm{s}}{F^2 I}}$$

This is the length across which electric fields are screened. It is called the *Debye length*. This is a very short length in electrolyte solutions: for a typical ionic strength, it is of the order of 1 nm. *Electroneutrality* holds at distances much larger than 1 nm from a charged surface:

$$\sum z_i c_i = 0$$

The constraint of electroneutrality can be used as a condition determine the electric potential in the Nernst–Planck equations, in place of the full Poisson equation. The Nernst–Planck equations with electroneutrality are used to describe current flow in the **Tertiary Current Distribution, Nernst-Planck** interface.

⚲
The Tertiary Current Distribution, Nernst–Planck Interface

The current flow itself is given by

$$\mathbf{i}_l = F \sum z_i \mathbf{N}_i$$

From substitution of the Nernst–Planck expressions for $\mathbf{N}_i$, the laws of conservation of mass and charge combine to automatically satisfy conservation of current.

We can simplify the system further by considering the arising expression for $\mathbf{i}_l$ in more detail:

$$\mathbf{i}_l = -F \sum D_i z_i \nabla c_i - \frac{F^2}{RT} \nabla \phi_l \sum z_i^2 D_i c_i + \mathbf{u} \sum z_i c_i$$

Clearly, the rightmost term is zero: that is, convection of an electroneutral solution does not cause current flow. The leftmost term (diffusion current) also vanishes due to electroneutrality if the gradients of the charge carrying species are zero.

Even if this is not the case, however, this term is often much smaller than the central term (migration current), so long as the concentrations of the current-carrying ions do not vary markedly through the solution. Under conditions where the composition of the electrolyte can be considered nearly constant and current-carrying ions are not significantly depleted, the diffusion current can be assumed to contribute negligibly.

Hence, it follows that

$$\mathbf{i}_l = -\sigma_l \nabla \phi_l$$

This expression for current density is used in the **Secondary Current Distribution** interface, and also the **Primary Current Distribution** interface. The difference between these interfaces lies in the treatment of the electrode-electrolyte interfaces (see Kinetics of Electrochemical Reactions below). From the above, the conductivity of the electrolyte σ_l is given as:

$$\sigma_l = \frac{F^2}{RT} \sum z_i^2 D_i c_i$$

So long as this quantity does not vary markedly through the solution, the approximation of zero diffusion current is good. If the diffusivities and concentrations can be taken as constant, we can approximate that:

$$\sigma_l \approx \frac{2F^2 I D_{mean}}{RT}$$

The advantage of the ohmic expression for current density is that it is a linear relation of current density to electrolyte potential. It is only weakly nonlinear if σ_l is allowed to depend on a concentration solved for in a species transport interface. By comparison, the Nernst–Planck equations with electroneutrality can be highly nonlinear.

The approximations used to derive the secondary current distribution expression place tighter constraints on the allowed system configurations, however. The ionic strength of the solution must remain near-constant for the constant conductivity approximation to be valid. Usually this is only the case for relatively high conductivity solutions.

When the conductivity is large with respect to the current drawn, the electric field becomes negligible in solution. For negligible electric fields, a diffusion-only approximation may be used, where $\mathbf{E} = \mathbf{0}$. This converts the Nernst–Planck equations into Fick's laws, with a term for convective transport where necessary. Fick's laws with convection and electrochemical boundary conditions are solved for in the **Electroanalysis** interface.

	Even if you think a problem will involve the full Nernst–Planck equations, it is best to set the model up in **Secondary Current Distribution** first, in order to identify any other possible complications in the system while using a simpler electrochemical model.

	Theory for the Current Distribution Interfaces

Modeling Electrochemical Reactions

Electrochemical reactions are defined by using **Electrode Reaction** or **Porous Electrode Reaction** nodes. An electrode reaction is defined by its thermodynamics, kinetics, and stoichiometry. The latter describes the mass fluxes, sources, and sinks arising due to a certain current density of the reaction.

THERMODYNAMICS OF ELECTROCHEMICAL REACTIONS

An electrolytic reaction involves the exchange of electrons with the electrode. Such a reaction is written as reduction, even if the reaction occurs predominantly in the oxidative direction. For example:

$$Ag^+(aq) + e^- \leftrightarrow Ag(s)$$
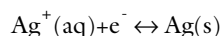
This reaction is called a "half-cell" reaction, since it will occur at a specific electrode-electrolyte interface. It cannot occur in isolation, but only when coupled to another half-cell reaction within a two-electrode electrochemical cell. Each reaction has a characteristic Gibbs energy change that determines whether or not it is thermodynamically favorable. A negative Gibbs energy change means that the reaction proceeds spontaneously — it is thermodynamically "downhill".

The Gibbs energy change is related to the equilibrium potential difference from the electrode to the electrolyte according to:

$$E_{eq,m} = -\frac{\Delta G_m}{n_m F}$$

where $E_{eq,m}$ is the potential difference on some external reference scale for which the reaction is at equilibrium ($\Delta G = 0$). This is called the *equilibrium potential* or *reduction potential* (or in corrosion, *corrosion potential*) of the electrochemical reaction, and its absolute value depends on the choice of reference electrode.

⚠️ Equilibrium potentials should always be quoted versus a specific reference. If a different reference scale is used in different parts of your model, the thermodynamics of the system may not behave as expected.

From the standard thermodynamic relation

$$\Delta G = -RT \ln K$$

it follows that

$$E - E_{eq} = \frac{RT}{nF} \ln K$$

This is the Nernst equation which is a universal thermodynamic expression. It is always true of systems at thermodynamic equilibrium; it does not necessarily apply to systems not at equilibrium.

Assuming that the species are ideal and that activity effects can be treated as constant, then for the conversion between unimolecular reduced and oxidized species:

$$[Ox] = [Red]\exp\left(\left(\frac{nF}{RT}\right)(\phi_s - \phi_l - E_f)\right)$$

Hence at *equilibrium*, the concentrations of reactants and products at the *electrolyte-electrode surface* are related by an expression which depends on the potential difference between the two phases, and two reaction parameters: n, the number of electrons transferred per molecule reduced; and E_f, the formal reduction potential of the reaction measured on the same potential scale as the electrode-electrolyte potential difference.

The quantity

$$\eta_m = \phi_s - \phi_l - E_{\text{eq},m}$$

is known as the *overpotential* and is particular to a specific reaction occurring at the interface.

η_m depends on both the electric potential in the electrode ϕ_s and the electrolyte potential ϕ_l. Where there is substantial resistance to current flow through a solution, the corresponding potential difference in ϕ_l called *ohmic drop*, alters the position of the electrochemical equilibrium. Additional applied potential in the electrical circuit may then be needed to drive an equivalent overpotential.

KINETICS OF ELECTROCHEMICAL REACTIONS

The Nernst equation tells us the position of equilibrium of a reaction. However, it tells us nothing about how fast the system may get there. If there is a kinetic limitation — that is, if the reaction proceeds slowly — the equilibrium condition may never be observed. As a familiar example, diamond is thermodynamically unstable with respect to reacting to form graphite at room temperature and pressure. However, this reaction is kinetically limited by a vast activation energy for the reorientation of atoms, such that it is never in practice observed, and diamond is technically described as *metastable*.

We encounter the same issue in many electrochemical contexts. Reactions are prevented from proceeding to their equilibrium by kinetic limitations. Indeed, overcoming the natural kinetic sluggishness of the surface reactions of small, nonpolar molecules such as hydrogen and oxygen is key to much fuel cell research.

There are two important expressions describing the current density due to an electrochemical reaction as a function of the overpotential and the concentrations of reactant and product. It should be noted that the validity of these expressions is not general and can never replace experimental kinetic data if such is available.

The first is the *Tafel law* which describes an irreversible anodic or cathodic process:

$$\log\left(\frac{i}{i_0}\right) = A\eta$$

The constant A is the *Tafel slope* and has units $1/V$. It is usually close to a half-integer multiple of F/RT and is less than or equal to nF/RT. Note that a reference *exchange current density* i_0 must be specified for the reaction. This is by definition the current density drawn at zero overpotential.

⚠️ The Tafel law assumes that a reaction is irreversible. If the reverse reaction might occur in practice, Tafel kinetics will not be correct.

The second expression is the *Butler–Volmer equation*, which describes a reversible process, so that either anodic or cathodic current may flow depending on the sign and magnitude of the overpotential:

$$i = i_0\left(\exp\left(\frac{\alpha_a F\eta}{RT}\right) - \exp\left(\frac{-\alpha_c F\eta}{RT}\right)\right)$$

The Butler–Volmer equation is the most general description of electrode kinetics. It is highly adaptable because:

- i_0 is an empirical quantity.
- It agrees with the Nernst equation when $i = 0$, so for a very fast reaction ($i_0 \to \infty$) then the Butler–Volmer equation gives the same potential difference as the Nernst equation. This is equally true under high resistance conditions.
- It agrees with the Tafel equation when either the anodic or cathodic term dominates. For highly irreversible reactions (very low i_0), appreciable current is only drawn for large overpotential, so this is typically the case.

For a discussion on the Butler–Volmer expression and concentration changes of the participating species, see the Defining Concentration Dependent Butler–Volmer Kinetics section below.

For a reversible reaction at very low overpotential (η of order $RT/F \sim 25$ mV), the exponentials in the Butler–Volmer equation can be linearized:

$$i_{\text{loc}} = i_0\left(\frac{(\alpha_a + \alpha_c)F}{RT}\right)\eta$$

	Using a linearized Butler–Volmer reaction can be advantageous when investigating convergence issues of a model.
⚠	The linearized Butler–Volmer equation is not correct for applied overpotentials larger than (RT/F). This is about 25 mV at room temperature. It is not suitable outside this range and therefore its use is confined to electrochemical processes occurring exclusively at low current density, such as electroplating or electrochemical impedance spectroscopy.

⊙	Electrode Kinetics Expressions

FLUXES AND SOURCES/SINKS DUE TO ELECTRODE REACTIONS

Electrode reactions will result in a molecular flux of reacting species to or from the electrode surface. If you are including mass transport in your model it is common to couple the flux of a reacting species on a boundary to the electrode reaction current density (by the Faraday's law of electrolysis).

The coupling of chemical flux to electric current density is automated in some of the Electrochemistry interfaces by defining the reaction stoichiometry in the **Electrode Reaction** and **Porous Electrode Reaction** nodes. In the Chemical species transport interfaces the coupling however needs to be set up manually by the Electrode Surface Couplingnodes. When modeling porous electrodes, the corresponding coupling node to create a source/sink in a domain is the Porous Electrode Coupling node.

The mathematical treatment can be summed up by the expression:

$$N_j = -\frac{v_{jm} i_m}{n_m F}$$

This means that the flux N_j of chemical species j into the surface is proportional to the current density i_m due to reaction m drawn at an electrode-electrolyte interface. The constant of proportionality is the stoichiometric number for the species divided by n_m, the number of electrons transferred in reaction m, in a reductive direction and F the Faraday constant (96,485 C/mol, the absolute charge on a mole of electrons).

As such, knowledge of the stoichiometry of an electrochemical reaction allows the local flux of a chemical species to be coupled to the current density contributed by that reaction. Note that multiple reactions may take place simultaneously at an electrode, and their contributions to the current density are simply summed.

💡	The stoichiometric coefficients of the chemical species in an electrochemical reaction are conventionally written with the forward reaction in the direction of reduction, even if in practice within the system the reaction predominantly proceeds in the other direction.
❗	COMSOL Multiphysics uses the standard convention that anodic (oxidative) current is positive. Cathodic (reductive) current is negative.

DEFINING CONCENTRATION DEPENDENT BUTLER–VOLMER KINETICS

If the concentrations at an electrode surface change, this will have an impact on the local kinetics. The Butler–Volmer kinetics expression is derived by considering the rate of a redox reaction

$$Ox + ne^- \leftrightarrow Red \tag{2-1}$$

as the sum of the forward and backward rates according to:

$$r = \frac{i_{loc}}{nF} = k_{fwd}c_R \exp\left(\frac{\alpha_a FE}{RT}\right) - k_{rwd}c_O \exp\left(-\frac{\alpha_c FE}{RT}\right) \tag{2-2}$$

where k_{fwd} and k_{rwd} are reaction rate constants and c_O and c_R are the activities of the oxidized and reduced species of the redox couple, respectively. The potential E is here defined as

$$E = \phi_s - \phi_l \tag{2-3}$$

and the transfer coefficients are equal the sum of electrons in the charge transfer reaction according to

$$\alpha_a + \alpha_c = n \tag{2-4}$$

By defining an equilibrium potential at which the forward reaction and backward reaction rates are equal, Equation 2-1 can be shown to be equivalent to the commonly used Butler–Volmer equation:

$$i_{\text{loc}} = i_0\left(\exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(-\frac{\alpha_c F \eta}{RT}\right)\right) \qquad (2\text{-}5)$$

In this formulation, assuming the stoichiometric coefficients of the oxidized and reduced species to be -1 and 1, respectively, the exchange current density, i_0, is defined as:

$$i_0 = i_{0,\text{ref}}\frac{c_R}{c_{R,\text{ref}}}^{\alpha_c/n}\frac{c_O}{c_{O,\text{ref}}}^{\alpha_a/n} \qquad (2\text{-}6)$$

where $i_{0,\text{ref}}$ is the exchange current density at some chosen reference conditions, and the overpotential is defined as

$$\eta = E - E_{\text{eq}} \qquad (2\text{-}7)$$

where E_{eq} is the equilibrium potential is defined by the Nernst equation as

$$E_{\text{eq}} = E_{\text{eq,ref}} - \frac{RT}{nF}\ln\frac{c_R/c_{R,\text{ref}}}{c_O/c_{O,\text{ref}}} \qquad (2\text{-}8)$$

and $E_{\text{eq,ref}}$ is the equilibrium potential at the same reference conditions.

Typically standard conditions are used as reference concentrations, for instance concentrations of 1 M for ions in aqueous solutions.

Note that in Equation 2-5 *both* i_0 and E_{eq} are concentration dependent. This has some numerical drawbacks when modeling electrochemical cells including mass transport, since for low concentrations of the participating species (that is, when $c_O \to 0$ or $c_R \to 0$), the factor $\ln(c_R/c_O)$ may become undefined during the solution process. An expression of the form of Equation 2-2 is more desirable since this expressions contains a simple linear dependence on the species activities.

A common solution to this issue is to rewrite the Butler–Volmer expression by defining the overpotential with respect to a fixed reference state for the activities $c_{R,\text{ref}}$ and $c_{O,\text{ref}}$ (typically corresponding to the inlet or initial concentrations), resulting in

$$i_{\text{loc}} = i_{0,\text{ref}}\left(\frac{c_R}{c_{R,\text{ref}}}\exp\left(\frac{\alpha_a F \eta_{\text{ref}}}{RT}\right) - \frac{c_O}{c_{O,\text{ref}}}\exp\left(-\frac{\alpha_c F \eta_{\text{ref}}}{RT}\right)\right) \qquad (2\text{-}9)$$

where

$$\eta_{\text{ref}} = E - E_{\text{eq,ref}} \qquad (2\text{-}10)$$

Note that Equation 2-9 now contains a linear dependence on the activities c_O and c_R.

Double Layer Capacitance

The Tafel and Butler–Volmer expressions can be used to calculate the magnitude of the current due to electrolysis: this is called *faradaic current*. However, the electrode-electrolyte interface may also draw capacitive current due to the attraction or repulsion of ions creating an oppositely charged layer of ions to form in solution close to the electrode.

The layer of charge on the electrode and layer of opposite charge in the adjacent electrolyte is called the *double layer* and can be thought of as behaving like a parallel plate capacitor, since the absolute amount of charge it separates varies with the charge density on the electrode, and hence with its voltage. The physics of double layer structure and formation are highly complex and are not yet well understood. One of the simplest empirical methods to account for the observed influence of capacitance on polarization curves is to introduce a constant ideal capacitance across the electrode-electrolyte interface.

This effect can be added to via the **Double Layer Capacitance** condition. The capacitor stores a surface charge density $Q = C_d(\phi_s - \phi_l)$, and contributes a dynamic charging current density (*nonfaradaic current*) equal to $i_{NF} = dQ/dt$. The total current recorded in a real experiment equals:

$$i_{tot} = i_{Far} + i_{NF}$$

Sometimes in electroanalysis a blank scan with no electrolysis is run to subtract nonfaradaic current. If double layer capacitance is ignored in your model, you should make sure that you are comparing it to experimental data recorded under the same conditions.

> ⚠ The ability of COMSOL Multiphysics to model electrostatics and transport of charged species make it tempting to incorporate the double layer explicitly to add more detail to a model. These coupled equations are always extremely nonlinear and convergence is not trivial except in the simplest cases. Although the diffuse double layer can be modeled in isolation (see example), this is not recommended in conjunction with a fuller electrochemical model.

🔍	Double-Layer Capacitance

Porous Electrodes

A porous electrode is one in which the three-dimensional structure of the electrode is permeable to electrolyte. The electrode-electrolyte interface then extends over a much larger surface area. This specific surface area ("SSA", area per unit volume, units $1/m$) is a key property of a porous electrode. Additionally, such an electrode can conduct electrical current independently through its electrode and electrolyte domains.

Most electrochemical interfaces in COMSOL Multiphysics include **Porous Electrode** domain nodes that can be used to model the above situation. In a **Porous Electrode**, current density is carried in both the electrode and in the pores which are assumed to contain electrolyte. For gas diffusion electrodes where the solid is conducting but the pore phase is not, the **Electrode** condition should be used.

It is common to combine an electrochemical interface with other physics, in order to model the mass transport, heat transfer and flow properties of a porous medium. For instance, **Secondary Current Distribution** might be coupled to **Transport of Diluted Species in Porous Media**, **Heat Transfer in Porous Media**, and **Darcy's Law**.

⚠️	Homogenized transport parameters such as diffusion coefficients are commonly obtained for a bulk solution of the material. In porous media these must be corrected for tortuosity and porosity. Carefully consider such effects when defining your material properties.
🔍	Porous Electrode Theory

Boundary Conditions for Running and Controlling Electrochemical Cells

An electrochemical cell is typically operated by controlling either the cell voltage (potentiostatic control) or the cell current (galvanostatic control). In a lab experiment this is accomplished by using a potentiostat.

In a model, potentiostatic control is defined by using fixed potential boundary conditions. This can be done by setting the **Electric Potential** with respect to ground to

control the cell potential, or the **Electrode Potential** with respect to a reference potential somewhere in the system. Galvanostatic control can be accomplished using **Total Current** or **Average Current Density** boundary conditions. For both cases, one electrode in the cell needs to be grounded.

Mathematically, a **Total Current** or **Average Current Density** condition implies setting the potential of a boundary to be equal to an additional extra global potential degree of freedom (floating potential) to comply with the specified current condition. For this reason, solving for galvanic control is numerically slightly more complex.

Note that explicitly prescribing the current density distribution on an electrode boundary is hard to accomplish in a real world experiment. In higher dimensions than 1D, **Electrode Current Density** and **Electrolyte Current Density** boundary conditions should be used with care.

SHORT-CIRCUITING A CELL AND GALVANIC CORROSION

The simplest way to model a short-circuited cell is to set both electrodes to the same (electronic) potential, using a fixed potential boundary condition. The charge balance equation of the electrolyte will make sure the total current over all electrode surfaces sums up to zero.

Note that many galvanic corrosion situations are practically equivalent to a short circuit of two electrodes consisting of different metals. In such models, the two metals are set to the same potential. Usually this potential is chosen to be zero (ground).

	• Electrode Potential
🔍	• Reference Electrode

Modeling Cyclic Voltammetry

In a cyclic voltammetry experiment, a potentiostat is used to sweep the voltage at the working electrode linearly from a start potential to a vertex potential, and back again. Typically, the potential window is chosen to span the formal potential of a redox couple of interest, allowing both the kinetics and transport properties of the chemical species to be investigated. The target species reacts under kinetic control to the point of depletion where the current becomes transport-controlled.

The built-in **Cyclic Voltammetry** study step in the **Electroanalysis** interface can be used to automatically set up the voltage sweep in a time-dependent study.

SHOULD I MODEL IN 3D OR CAN I MODEL IN 1D?

Many electrochemical systems use repetitive unit cells of high aspect ratio. In these cases, the lumped effect of edge phenomena in the system will be small. For example, in fuel cells or batteries it is often possible to use one-dimensional geometries with little loss of detail. Consider also any mirror or rotational symmetries. Reducing the geometry dimension where possible, either exactly or approximately, will reduce the meshing and solving time significantly.

	Starting with a 1D model helps to understand the influence of different reactions and phenomena in an electrochemical system, and gives a good first estimate of current-voltage behavior.

NEGLECTING THE CHARGE TRANSFER AND POTENTIAL GRADIENTS IN ELECTRODES

The voltage over the surface of an electrode is typically constant — or very nearly constant — since it is a good conductor. This implies that it is either the intrinsic resistance of the electrolyte or the rate of the electrochemical reaction at the electrode-electrolyte interface that controls the amount of current drawn in an electrochemical cell. On the assumption of a constant surface voltage, the electrode domain itself need not be modeled, and the coupling of charge and mass transport at its surface treated by an **Electrode Surface** node.

	Electrode Surface

However, when modeling porous and gas diffusion electrodes the metal phase potential is need typically to be included since the conductivity of the metal phase potential can be much lower in this type of electrodes. This is done in the **Porous Electrode** nodes.

HALF-CELL MODELS

Often, an investigator is only interested in the chemistry taking place at one electrode in a cell. A model of one electrode is called a "half-cell model".

This would correspond to an experimental situation where the electrode of interest — be it anode or cathode — is classified as the *working electrode*, and the other electrode is called the *counter electrode*.

One usually ignores the kinetics of the counter electrode in a model; commonly it is represented by a constant potential boundary condition. Such a model is only valid if the counter electrode can draw arbitrarily large amounts of current compared to the working electrode, so that it never limits the current flow in the electrochemical cell.

REPLACING THIN LAYERS WITH BOUNDARY CONDITIONS

When considering a layer that is very thin compared to other dimensions in the geometry, it is usually correct to treat that layer using a physical condition, rather than meshing it.

One important example is the catalyst layer in a fuel cell. Since this layer is only nanometers in size, transport across it is very fast compared to other parts of the system. Hence, it is not necessary to resolve a distribution of concentrations or potentials through the layer.

Another example is the passivation layer on an oxidized electrode surface, for which the "Thin Film Resistance" setting can be used. Because the layer is much thinner than its surroundings, the electric field through it is almost constant. Therefore, an ohmic expression can be substituted to create a boundary condition with a potential drop. This is much more efficient than meshing a geometrically narrow layer.

🔍	Film Resistance

INFINITE ELEMENTS FOR STEADY-STATE ELECTROANALYSIS

For microelectrodes, the diffusion profile may approach a steady state whose size is much larger than that of the working electrode of interest. In such an example, it is preferable to circumscribe the simulation space to a region not more than about twenty-five times the electrode size - assuming that the surrounding electrolyte is uniform. Applying a bulk boundary condition such as a fixed concentration at this finite distance causes inaccuracy in the solution, however.

It is better to use a layer of **Infinite Elements** around the finite simulation space to project the simulation space to infinity, eliminating any error from artificially limiting the simulation space. This is a typical approximation when the electrolyte domain is a

few orders of magnitude larger than the electrode: for example, a microelectrode in a cm-scale reaction vessel.

🔍	Infinite Elements, Perfectly Matched Layers, and Absorbing Layers in the *COMSOL Multiphysics Reference Manual*

Before You Start Building Your Model

INTRODUCING COMPLEXITY ONE STEP AT A TIME

The true art of modeling is knowing what phenomena to include and what phenomena to neglect. Building complexity in a model by adding one additional piece of physics or geometric feature at a time is usually the fastest way to reach the modeling goal. Here are some general tips:

- Start thinking about your cell in the lowest possible dimension. Starting with a 1D model helps to understand the influence of different reactions in an electrochemical system, and gives a good first estimate of current-voltage behavior. Go from 1D to 2D, then from 2D to 3D.

- Every electrode reaction adds numerical nonlinearities to your model. If you have multiple electrode reactions, add them one at a time.

- Start with a simple description of the electrolyte current, such as **Secondary Current Distribution**. Analyze the results to ensure that the electrochemical model is consistent. Switch only to more complex electrolyte models, or add extra physics such as mass transfer, heat transfer or flow, only if deemed necessary and when satisfied with the results from a simpler case.

- If you are including flow in your model, solve for the flow field first before coupling flow and electrochemistry together.

MODELING CHECKLIST

- Identify which domains are electrode and electrolyte. How will their conductivity be assessed?

- What is happening on the electrode-electrolyte interfaces? Do both the anode and the cathode need to be modeled? Do either need to be modeled as domains, or can they be treated as boundaries?

- What electrochemical reactions take place at the electrode surfaces to cause charge transfer? Can you parameterize their thermodynamics? Do you know the

equilibrium potentials? Can you parameterize their kinetics — and are the kinetics ever going to be important? If not, ignore them.

- What is the system reference potential used to quote equilibrium potentials? Where is the system ground?

- Are charge carriers in the electrolyte plentiful with respect to the drawn current density, or is charge depletion important? Be aware of nonlinear effects that may make convergence more difficult.

- If you are performing a time-dependent study, do your initial conditions have a consistent current-voltage relationship?

- What other physics interfaces need to be coupled? How does charge transfer influence these physics interfaces?

Meshing Advice

The default triangular (2D) or tetrahedral (3D) mesh is normally suitable for solving the equations describing conservation of charge and mass for a general electrochemical problem.

Electrochemical models involving mass transport generally benefit from a finer mesh at the electrode surfaces, and at singularities such as the boundary between an electrode surface and an insulating surface. This may be accomplished by adding additional **Size** mesh nodes for these boundaries only. Also, consider refining the "element growth rate", and/or using boundary layer meshing in 3D.

Sometimes, a regular **Mapped** mesh can be more appropriate in a rectangular (2D) domain; such domains are common in cutaway schematic studies of batteries and fuel cells. Similarly the **Swept** mesh is often appropriate for very thin layers in a 3D model.

For fluid domains, the default physics-controlled mesh should be used, with boundary layers as required.

For some problems with a stationary flow velocity field and time-dependent convection of electrochemically reacting species, it may improve convergence to set up a refined mesh without boundary layers for the species transport study step.

Q	Meshing in the *COMSOL Multiphysics Reference Manual*

Solving Electrochemical Models

Due to the highly nonlinear nature of electrode kinetics, some electrochemical models can be difficult to solve. This section includes some general tips and tricks to facilitate model solving, trouble shooting, and to improve solution accuracy.

GENERAL CURRENT DISTRIBUTION PROBLEMS

Start with the following suggestions if you encounter difficulty solving a problem.

- Make sure that the potential levels are "boot-strapped" somewhere in the model, preferably by grounding one electrode. If there is no potential level defined anywhere in the model, your model may have infinitely many solutions, and the model will not converge.

- Consider using a **Stationary with Initialization** or a **Time Dependent with Initialization** study. Both these studies will use a **Current Distribution Initialization** study step as a first step to solve for the potentials only. If you run into problems solving for the second step in this study you may have to change the "Current distribution type" setting to **Secondary** on the **Current Distribution Initialization** study step node, and also review the **Initial Values** as described in the next bullet.

- Review the **Initial Values**, especially the potentials. Suitable initial potential values can usually be derived making a "potential walk" through the geometry, starting at the grounded boundary. Compute electric and electrolyte potentials in other domains by assuming equilibrium potential differences between electrode and electrolyte for the main electrode reactions.

- Switch to **Linearized Butler-Volmer** kinetics (or a **Primary** current distribution) while troubleshooting. This can be useful to help achieve a solution for a model that does not solve with nonlinear kinetics, thereby indicating suitable initial values for the nonlinear problem.

- If your model contains porous electrodes, try refining the mesh resolution in these domains, especially toward the electrolyte boundaries.

ℚ	• Electrochemistry Interfaces
	• Specifying Initial Values and Inspecting and Troubleshooting Meshes in the *COMSOL Multiphysics Reference Manual*

If the model involves electrochemistry coupled to mass transport, here are a few things to try to help improve model convergence.

- Review the **Initial Values** for the concentration values. Zero initial concentration values can be unsuitable for tertiary current distribution problems and battery simulations, since they could imply that no charge carriers or no reacting material is present.

- If steep concentration gradients are expected close to electrode surfaces, use boundary layer meshing or finer mesh **Size** settings at these boundaries.

- When setting up user-defined kinetics expressions, avoid evaluating negative concentrations by using expressions such as `max(c, eps^2)`, where `eps` is the machine epsilon (a very small but finite number).

- Try to solve for low currents and low overpotentials first, then increase the cell load (for stationary problems this can be done using an auxiliary sweep with continuation).

- If a problem involving mass transport is hard to solve for high currents, but solves for low currents, it might be due to mass transport limitations. In this case, review the transport parameter values and check that the current magnitudes are reasonable. If the current densities are unreasonably high, review the electrode reaction settings.

- For time-dependent problems that run into convergence problems after a certain time, review the solution at the last time-step. If the solution of a reactant reaches zero or a maximum value (for insertion electrodes in batteries) when the convergence issues occur, the current load of the model is too high in relation to your initial concentrations or mass transport properties.

Q
- Electrochemistry Interfaces

In the *COMSOL Multiphysics Reference Manual*:

- 2D and 3D Boundary Layer Meshes
- Stationary and Parametric Sweep

SETTING UP A STUDY SEQUENCE FOR MULTIPHYSICS PROBLEMS

For multiphysics problems, try to adjust the study sequence.

- Solve certain physics interfaces in a sequence. This can in many cases reduce computational time and improve convergence. Analyzing the results when solving a

physics interface separately can also help when troubleshooting a nonconverging model.

- A good strategy is often to solve for the potentials only (that is, disable mass transport and flow interfaces), using a stationary study step, before solving the full model in the study sequence. In this way the stationary solution is used as initial values for the following steps. This can be manually by modifying the settings of the study node, or in an automated way by using the **Stationary with Initialization** or **Time Dependent with Initialization** study sequences, as described above.

- In many models the flow profile is only slightly (or not at all) affected by changes in current density. Therefore it can be a good strategy to solve separately for the flow early in the study sequence, and then solve for the other physics interfaces in the subsequent steps. (If the flow is not affected at all by the current distribution, solving for the flow can be disabled entirely in consecutive steps.)

$\mathbb{Q}$

- Electrochemistry Interfaces

  In the *COMSOL Multiphysics Reference Manual:*

- Studies and Solvers
- Analyzing Model Convergence and Accuracy
- Achieving Convergence When Solving Nonlinear Equations

TIME-DEPENDENT PROBLEMS WITH LOAD STEPS

For time-dependent problems, try the following to address accuracy and convergence issues with regards to sudden current or potential load steps.

- Use smoothed current or potential load functions in order to avoid instantaneous or discrete load steps.

- Add a double layer capacitance to the model, which can improve the numerical stability.

- Reduce the **Maximum step** taken by the solver if you want to prevent the solver from "missing" short square load steps, or change the **Steps taken by solver** setting from **Free** to **Strict**, or **Intermediate**, to control the time steps using the **Times** text field.

Using the Events interface can also be an option in certain cases if the load cycle itself varies dynamically.

	• Double-Layer Capacitance
🔍	In the *COMSOL Multiphysics Reference Manual:*
	• Step and Time Dependent
	• Building a COMSOL Multiphysics Model and The Events Interface

SOLVER SETTINGS

Try adjusting the solver settings.

• In rare cases, try to increase the **Maximum number of iterations**.

• If you know the order of magnitude of the dependent variables beforehand, setting the scaling method to **Manual** for these can improve convergence and the accuracy of the results. This may be of special importance when solving for concentrations that are initially very small but where the final order of magnitude is know *a priori*. This could be the case for the active species in a battery model, for example.

	In the *COMSOL Multiphysics Reference Manual:*
🔍	• Studies and Solvers
	• Analyzing Model Convergence and Accuracy
	• Achieving Convergence When Solving Nonlinear Equations

🔍	Electrochemistry Studies and Study Steps and Cyclic Voltammetry in the *COMSOL Multiphysics Reference Manual*

⚠️	In multicomponent systems it is rarely straightforward to predict the rest potential and direction of current flow. The **Current Initialization** step in COMSOL Multiphysics does this for you but is only correct if concentrations and formal potentials for all electrode reactions are specified precisely and with respect to a common reference scale.

Postprocessing Your Solution

POTENTIAL VARIABLES

Several different potential variables are available for postprocessing and during computation. The most common ones are described in Table 2-1.

TABLE 2-I: COMMON POTENTIAL VARIABLES.

VARIABLE	DESCRIPTION	DEFINED AT
phil	Electrolyte phase potential	Electrolyte and Porous Electrode domains
phis	Electrode phase potential	Electrode and Porous Electrode domains
xxx.phisext	Electrode phase potential	Electrode Reaction boundaries to Electrolyte domains
xxx.Eeq_yy	Equilibrium potential	Electrode Reaction boundaries and Porous Electrode Reaction domains
xxx.eta_yy	Overpotential	Electrode Reaction boundaries

The unit is V for all the above variables.

xxx denotes the tag of the physics interface. For instance, **cd** for the Secondary Current Distribution interface.

yy denotes the tag of the (Porous) Electrode Reaction node, for instance, **er1** for an Electrode Reaction node.

CURRENT VARIABLES AND CALCULATING THE TOTAL CELL CURRENT

The current density may vary between locations on an electrode surface. This effect is very important to understand through modeling because it cannot be directly measured. Experimental measurement can only return the total current drawn at an electrode, although the variation in current density can be inferred by other means.

To calculate the total current in COMSOL Multiphysics, it is necessary to integrate the total drawn current density along the boundary or over the domain of the electrode. Some common current density variables are shown in Table 2-2.

TABLE 2-2: COMMON CURRENT DENSITY VARIABLES.

VARIABLE	UNIT	DESCRIPTION	DEFINED AT
xxx.nIl	A/m^2	Electrolyte current density in normal direction	Boundaries to Electrolyte and Porous Electrode domains
xxx.nIs	A/m^2	Electrode current density in normal direction	Boundaries to Electrolyte and Porous Electrode domains
xxx.iloc_yy	A/m^2	Local current density of electrode reaction	Electrode Reaction boundaries
xxx.itot	A/m^2	Total interface current density (local sum of all xxx.iloc_yy)	Electrode Reaction boundaries
xxx.iv_yy	A/m^3	Volumetric current density of a Porous Electrode Reaction	Porous Electrode domains
xxx.ivtot	A/m^3	Total volumetric current densities (local sum of all xxx.iv_yy)	Porous Electrode domains
xxx.llMag	A/m^2	Electrolyte current density magnitude (L^2 norm)	Electrolyte domains
xxx.lsMag	A/m^2	Electrode current density magnitude (L^2 norm)	Electrode domains

xxx denotes the tag of the physics interface. For instance **cd** for the Secondary Current Distribution interface.

yy denotes the tag of the (Porous) Electrode Reaction node, For instance **er1** for an Electrode Reaction node.

In 1D or 1D axisymmetric, the electrode is implicitly uniform so you can just multiply by the area of the electrode. In 2D or 2D axisymmetric, compute the appropriate line integral. In 3D, compute the surface integral.

You can also define your own total current variable by using an **Integration** nonlocal coupling across the electroactive boundaries. This variable can also be used during the

computation. In 1D axisymmetric and 2D axisymmetric components, make sure to select the **Compute integral in revolved geometry** check box.

🔍	In the *COMSOL Multiphysics Reference Manual:* • Nonlocal Couplings and Coupling Operators and Integration
⚠️	Avoid evaluating the xxx.IlMag/xxx.IsMag variables on boundaries. These are generally less accurate than the xxx.nIl/xxx.nIs variables.

3

Fuel Cell and Electrolyzer Interfaces

This chapter describes the physics interfaces found under the **Electrochemistry>Hydrogen Fuel Cells** ( ) and **>Water Electrolyzers** ( ) branches.

In this chapter:

- The Hydrogen Fuel Cell and Water Electrolyzer Interfaces
- Theory for the Hydrogen Fuel Cell and Water Electrolyzer Interfaces

The Hydrogen Fuel Cell and Water Electrolyzer Interfaces

The **Hydrogen Fuel Cell** (fc) and **Water Electrolyzer** (we) physics interfaces are used to model the different electron and ion-conducting layers of various types of hydrogen fuel cells, or water electrolyzer cells. Optionally, gas phase transport and Darcy's law for convection in porous media and flow channels may be enabled and also solved for by the interfaces.

The interface supports simulation in 1D, 2D, and 3D as well as for axisymmetric components in 1D and 2D.

Note that once added to a model, the Hydrogen Fuel Cell (fc) and the Water Electrolyzer (we) interfaces are identical in terms of functionality and only differ by some default parameter values (see below), the default name (fc/we), and the icon (/).

The **Electrochemistry>Hydrogen Fuel Cell** ( ) and the **Electrochemistry>Water Electrolyzers** ( ) branches in the Model Wizard, or in the Select physics tab, contain a number of different entries for adding either a **Hydrogen Fuel Cell** (fc) or a **Water Electrolyzer** (we) physics interface, of different electrolyte types, to a model.

Depending on the selected entry, different species will be included by default in the electrode gas mixtures, and gas phase diffusion will be enabled by default if there are more than one species present a mixture. See also the H2 Gas Mixture and O2 Gas Mixture section below.

The chosen Model Wizard entry will also have an effect on the default stoichiometry and kinetics parameter values used when adding electrode reactions to the model. See the Electrode Reaction Settings below.

SETTINGS AT THE INTERFACE LEVEL (FC/WE)

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 `fc` for the Hydrogen Fuel Cell interface and `we` for the Water Electrolyzer interface.

DOMAIN SELECTION

If any part of the model geometry should not partake in the fuel cell/electrolyzer model, remove that part from the selection list.

H2 GAS MIXTURE AND O2 GAS MIXTURE

These sections specify what the species are present in the Gas Phase domains on the respective sides of the cell. Apart from hydrogen and oxygen, which are always assumed to be present on each side, you may here choose to include one or several of the species **H2O**, **N2**, **CO2**, and **CO** on each side. The species **CH4** may be included on the **H2** side. An additional, arbitrarily defined, gaseous species can be included on either side using **Auxiliary species**. The settings for the auxiliary species are found in the corresponding Gas Phase domain nodes.

If you expect concentration gradients in the gas diffusion electrodes (GDEs), gas diffusion layers (GDLs) or the flow channels, you may choose to **Include gas phase diffusion** in these sections. Gas phase diffusion can only be enabled if there are more than one species present in the gas mixture.

Use Darcy's law for momentum transfer for solving for the gas phase pressure using Darcy's Law in gas phase domains. This can be enabled individually for each gas mixture in these sections. Note, however, that instead of using the built-in Darcy's law of the `fc`/`we` interface, you can instead couple the interface to any Fluid Flow interface, or an analytical expression, by specifying the velocity explicitly in the Gas Phase nodes or by using an **Reacting Flow, H2/O2 Gas Phase** multiphysics coupling nodes.

If **Use H2O(l) in Reaction Stoichiometry** is enabled, this will allow for setting the stoichiometric coefficient of liquid water in electrode reactions, which in turn may be used for the built-in calculations of equilibrium and thermoneutral potentials. Unit activity of H2O(l) will be assumed in all expressions.

ELECTRODE REACTION SETTINGS

In this section you can control the default parameter settings that electrode reactions will get when added to the model, and how the potential of the global hydrogen reference electrode will be calculated.

The **Electrolyte type** setting (**Proton exchange**, **Hydroxide exchange**, **Molten carbonate**, **Solid oxide** or **Generic**) will impact the default stoichiometry of electrode reactions and
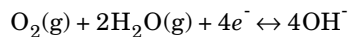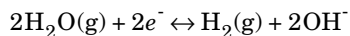
a built-in hydrogen reference electrode used for the calculation of equilibrium and thermoneutral potentials of the electrode reactions.

For all types except **Generic**, the **Reference hydrogen electrode equilibrium potential**, $E_{eq,RHE}$ (V), will be calculated using an internal database of reaction enthalpies and entropies, in combination with the **Reference hydrogen electrode temperature**, which should be a global value with no spatial dependency.

The **Generic** option will add no default stoichiometric coefficients, and for this case the $E_{eq,RHE}$ and the **Charge of the charge-carrying ion** will have to be specified explicitly.

Note that the **Entropy of the charge-carrying ion** has no impact on the equilibrium potentials vs $E_{eq,RHE}$, but will have an effect the calculation of the thermoneutral potentials. (See also Calculation of Built-in Equilibrium and Thermoneutral Potentials.)

The following reaction stoichiometry will be used for calculating $E_{eq,RHE}$, and as default for the electrode reactions on the H2 and O2 sides, respectively.

Proton exchange:

$$2H^+ + 2e^- \leftrightarrow H_2(g)$$

$$O_2(g) + 4H^+ + 4e^- \leftrightarrow 2H_2O(g)$$

Hydroxide exchange:

$$2H_2O(g) + 2e^- \leftrightarrow H_2(g) + 2OH^-$$

$$O_2(g) + 2H_2O(g) + 4e^- \leftrightarrow 4OH^-$$

Molten carbonate:

$$H_2O(g) + CO_2(g) + 2e^- \leftrightarrow H_2(g) + CO_3^{2-}$$

$$O_2(g) + 2CO_2(g) + 4e^- \leftrightarrow 2CO_3^{2-}$$

Solid oxide:

$$H_2O(g) + 2e^- \leftrightarrow H_2(g) + O^{2-}$$

$$O_2(g) + 4e^- \leftrightarrow 2O^{2-}$$

The **Operation mode** setting (**Fuel cell** or **Electrolyzer**) will impact the default values of the kinetics settings of added electrode reactions.

MEMBRANE TRANSPORT

In this section, transport of additional species (apart from the charge carrying ion) in Membrane domains may be enabled. The section is available if **Electrolyte type** setting is set to either **Proton exchange** or **Hydroxide exchange**.

The **Crossover species** include **H2**, **O2**, and **N2**. Note that the crossover species **N2** is available only if species **N2** has been selected in both the **H2 Gas Mixture** and the **O2 Gas Mixture**.

Electroosmotic water drag is available if the species **H2O** has been selected in both the **H2 Gas Mixture** and the **O2 Gas Mixture**.

REFERENCE PRESSURE LEVEL

This section is available if the **Use Darcy's law for momentum transport** check box has been selected. In this section, you specify the **Reference pressure level**.

CONSISTENT STABILIZATION

This section is available when **Stabilization** is selected in the **Show More Options** dialog box shown when the **Show More Options** button (👁) is selected.

The stabilization settings are applicable separately for the **H2 Gas Mixture** and the **O2 Gas Mixture** and are available if the corresponding **Include gas phase diffusion** check box is selected.

In convection-dominated parts of a cell where the mesh is not fine enough to resolve the concentration gradients, for instance in a boundary layer, stabilization may be added in order to avoid spurious oscillations in the solution, and to improve convergence. In fuel cells and electrolyzer cells, stabilization is more likely to be needed in the gas flow channels. In gas diffusion layers and gas diffusion electrodes stabilization is usually not needed due to the lower flow velocities. The stabilization expressions, particularly the crosswind diffusion expressions, may be costly to compute. Therefore, it is recommended to add stabilization only if needed, for instance when spurious gas mass fractions oscillations are observed in a solution.

There are two consistent stabilization methods available — **Streamline diffusion** (active by default) and **Crosswind diffusion** (inactive 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.

By default, **Streamline diffusion** stabilization, using an **Approximate residual**, is added **only to gas flow channels**. **Crosswind diffusion** stabilization, and computation of the **Full residual** may be turned on as required, in all domains.

ADVANCED SETTINGS

From the **Regularization** list, select **On** (default) or **Off**. When turned **On**, regularized mass fractions are selected such that they lie between 0 and 1. The regularized mass fractions are used in the calculation of composition-dependent material properties, such as density.

This section is available when the **Advanced Physics Options** is selected in the **Show More Options** dialog box shown when the **Show More Options** button (👁) is selected, in combination with the **Include gas phase diffusion** check box being selected.

PHYSICS VS. MATERIALS REFERENCE ELECTRODE POTENTIAL

The **Physics vs. Materials Reference Electrode Potential** setting on the physics interface node can be used to combine material library data for current densities and equilibrium potentials with an arbitrary reference electrode scale in the physics. The setting affects the electrode potentials used for model input into the materials node as well as all equilibrium potential values output from the materials node.

Note that the setting will only impact how potentials are interpreted in communication between the physics and the **Materials** node. If the **From material** option is not in use for equilibrium potentials or electrode kinetics, the setting has no impact.

This section is available when the **Advanced Physics Options** is selected in the **Show More Options** dialog box shown when the **Show More Options** button (👁) is selected.

OVERVIEW OF THE DOMAIN NODES IN THE HYDROGEN FUEL CELL AND WATER ELECTROLYZER INTERFACES

The following phase nodes are added as default nodes:

- Electrolyte Phase
- Electronic Conducting Phase
- Gas Phase (H2 and O2)

These default phase nodes define the physics in the different phases of the cell, and contain settings for, for instance, electrolyte conductivity and gas diffusion coefficients. Initial Values for the dependent variables defined by the phase nodes are available as subnodes. Boundary conditions for, for instance, potential, current densities, inflow gas compositions, and so on, are added as subnodes to the above phase nodes.

The default phase nodes have their selections locked to all domains, but may have their selections overridden by the following nodes, which may be added by the user:

- Membrane
- Separator
- Current Collector
- Gas Diffusion Electrode (H2 or O2)
- Gas Diffusion Layer (H2 or O2)
- Gas-Electrolyte Compartment (H2 or O2)
- Gas Flow Channel (H2 or O2)

These nodes define properties that do not pertain to the pure electrolyte or gas phases such as porosities, permeabilities, and electronic conductivities. Electrode reactions are added as subnodes to the gas diffusion electrode nodes.

Electrolyte Phase

The **Electrolyte Phase** node defines the governing domain equations for the electrolyte phase.

Note that this node is added by default, and that you cannot alter the selection of the node by settings on the node itself. The node will be active on domains selected by Membrane, Separator, Gas Diffusion Electrode or Gas-Electrolyte Compartment nodes.

ELECTROLYTE CHARGE TRANSPORT

The **Electrolyte conductivity**, σ_l (SI unit: S/m), parameter will define how the current in the domain depends on the gradient of the potential.

See also Electrolyte Phase Theory.

Electronic Conducting Phase

The **Electronic Conducting Phase** node defines the governing equations for the electronic conducting (electrode) phase.

Note that the node is added by default, and that you cannot alter the selection of the node by settings on the node itself. The node will be active on domains selected by Current Collector, Gas Diffusion Electrode or Gas Diffusion Layer nodes. The electronic conductivity, **Electrical conductivity**, σ_s (SI unit: S/m), used in the domain equations, is defined on these domains.

See also Electronic Conducting Phase Theory.

Gas Phase

The **H2 Gas Phase** and **O2 Gas Phase** nodes define the governing domain equations for gas phase transport.

Note that these nodes are added by default, and that you cannot alter the selection of the nodes by settings on the nodes themselves. The **H2 Gas Phase** and **O2 Gas Phase** are active on domains selected by the corresponding H2/O2 Gas Diffusion Electrode, Gas Diffusion Layer, Gas-Electrolyte Compartment or Gas Flow Channel nodes.

The **H2 Gas Phase** and **O2 Gas Phase** subnodes are only visible if the **Include gas phase diffusion** check box, or if the **Use Darcy's law for momentum transport** check box, are enabled in the corresponding **Gas Mixture** section on the interface top node.

COMPOSITION

This section is only visible if any of the **Include species** check boxes has been selected and the **Include gas phase diffusion** check box has not been selected in the physics interface top node.

Use **Mixture specification** to specify mixture composition in **Mole fractions** or **Humidified mixture** for all gas phase domains. The **O2 Gas Phase** node has an additional option of **Humidified air** for O2 gas phase domains.

The option **Mole fractions** is always available and text fields are used to specify the mixture composition for all included species.

Humidified mixture allows for specifying a gas mixture using values for a dry gas mixture, which is subsequently humidified to a specified relative humidity. The setting is available if H2O has been selected in the corresponding **Gas Mixture** section on the interface top node. Text fields are used to specify the mixture composition for all

included species except H2O. Additionally, the **Relative humidity**, **Humidification temperature** and **Humidification absolute pressure** of the humidifier are also specified.

Humidified air is available if H2O and N2 have been selected in the **O2 Gas Mixture** section on the interface top node. **Relative humidity**, **Humidification temperature**, and **Humidification absolute pressure** of the humidifier are also specified. The dry mole fractions of the included species are set internally as follows: 0.79 (N2), 4e-4 (CO2) and 1e-6(CO).

Given that the humidifier (inlet) temperature (T_{hum}), absolute pressure ($p_{A,hum}$) and relative humidity (RH_{hum}) of the humidifier (inlet) gases are known, the conversion from a set of dry (containing no water vapor) molar fraction to a corresponding humidified mixture may be calculated as follows. The water mole fraction is defined as

$$x_{H2O} = \frac{p_{vap}(T_{hum})}{p_{A,\,hum}} RH_{hum}$$

The wet mole fractions for all species except water are then calculated from the dry mixture molar fractions according to

$$x_i = x_{i,\,dry}(1 - x_{H2O})$$

MIXTURE PROPERTIES

In this section, the gas phase values for the **Density** and **Dynamic viscosity** are specified.

The mixture properties will for instance be used by the interface when modeling momentum transport by Darcy's law.

Note: Depending on the settings on the interface top node, the mixture property values may or may not be used by the interface itself. However, the interface will define mixture property variables that may be used when coupling to other physics interfaces, either manually or by multiphysics nodes such as **Reacting Flow, H2/O2 Gas Phase**. Additionally, the interface also defines liquid water properties (density and dynamic viscosity) in the H2/O2 Gas Phase domain nodes that may be used when coupling to other physics interfaces, if H2O has been selected in the corresponding **Gas Mixture** section on the interface top node.

CONVECTION

This section will only be visible if the **Use Darcy's law for momentum transport** check box has been selected in the interface top node.

Specify the **Velocity field** of the gas. The velocity field can be specified explicitly, or using an analytical expression, or coupled from any Fluid Flow interface, or by using an Reacting Flow, H2/O2 Gas Phase multiphysics coupling node.

DIFFUSION

This section will only be visible if the **Include gas phase diffusion** check box has been selected in the interface top node.

Specify the **Binary diffusion coefficients** for all pairs of species in the gas.

See also Gas Phase Theory.

AUXILIARY SPECIES

This section will only be visible if **Auxiliary species** check box has been selected in the interface top node.

Specify the properties of the auxiliary species, such as **Molar Mass**, **Molar standard enthalpy of formation**, **Molar standard entropy**, and **Molar heat capacity**. The **Fuller diffusion volume** is available if the **Include gas phase diffusion** check box has been selected in the interface top node and if using **Built-in Binary diffusion coefficients**. The **Dynamic viscosity**, **Thermal conductivity** and **Boiling point** are used for calculating the built-in gas phase dynamic viscosity and thermal conductivity, and are available if using **Built-in Dynamic viscosity**.

Membrane

The **Membrane** node specifies a domain with only an Electrolyte Phase node being active.

The electrolyte conductivity of the membrane is defined on the Electrolyte Phase node.

HYDROGEN/OXYGEN/NITROGEN CROSSOVER

These sections specifies the permeation (diffusion) of gases between the hydrogen and oxygen gas phase mixtures, across the membrane.

The **Crossover** sections for H2, O2, and N2, available if the corresponding crossover species has been selected in the **Membrane Transport** section on the interface top node,

can be used to specify the **Permeation coefficient** and the **Henry's law coefficient** of the corresponding species. The **Heat of reactions**, arising due to the parasitic reactions of H2 and O2 species, is available if H2 or O2 has been selected as crossover species. The **Thermoneutral voltage** is calculated automatically when the **Built in** option is used.

See also Membrane Crossover Theory.

ELECTROOSMOTIC WATER DRAG

This section specifies the water transport properties of the membrane. Water transport may occur both due to migration in the electric field and diffusion.

This section is visible if **Electroosmotic water drag** has been selected in the **Membrane Transport** section on the interface top node. The **Water transport model** can be selected as either **Vapor equilibrated** (default for fuel cells) or **Liquid equilibrated** (default for electrolyzers). The **Electroosmotic coefficient**, the **Water transport coefficient**, and the **Standard condition gas pressure** are specified in this section. The **Heat of water absorption** is available if **Electroosmotic water drag** has been selected.

See also Electroosmotic Water Drag Theory.

ELECTROLYTE WATER ACTIVITY FOR MATERIAL MODEL INPUT

This section is visible if **Electroosmotic water drag** has not been selected in the **Membrane Transport** section on the interface top node. The water activity specified in this section is used by the **Electrolyte Phase** node when using an electrolyte material that requires **Water activity (relative humidity)** as model input.

Separator

The **Separator** node specifies a domain with only an Electrolyte Phase node being active. This node is typically used to separate two Gas-Electrolyte Compartment domains of a liquid-electrolyte-based electrolyzer.

EFFECTIVE ELECTROLYTE CHARGE TRANSPORT

The bulk electrolyte conductivity defined in the Electrolyte Phase node will be multiplied by a correction factor to compensate for the effect of the **Electrolyte volume fraction** being less than 1. This can be done by either using a **Bruggeman**, **Tortuosity**, or **User defined** correlation. For **Tortuosity**, select either **Isotropic** to define a scalar value, or **Diagonal** or **Symmetric** to define anisotropic tensor values.

Current Collector

The **Current Collector** node specifies a domain with only the Electronic Conducting Phase node being active.

ELECTRODE CHARGE TRANSPORT

The electronic conductivity, **Electrical conductivity**, σ_s (SI unit: S/m) parameter will define how the electric current in the corresponding Electronic Conducting Phase domain depends on the gradient of the potential.

Gas Diffusion Layer

The **H2 Gas Diffusion Layer** and **O2 Gas Diffusion Layer** nodes specify domains where both an Electronic Conducting Phase and a Gas Phase node are active.

ELECTRODE CHARGE TRANSPORT

The effective electronic conductivity, **Effective electrical conductivity**, σ_s (SI unit: S/m) parameter will define how the electric current in the corresponding Electronic Conducting Phase domain depends on the gradient of the potential.

GAS TRANSPORT

This section will only be visible if the **Include gas phase diffusion** check box or the **Use Darcy's law for momentum transport** check box has been selected in the corresponding **Gas Mixture** section on the interface top node.

If the **Include gas phase diffusion** check box has been selected, the gas diffusivity defined in the Gas Phase node will be multiplied by a correction factor to compensate for the effect of the **Gas pore volume fraction** being less than 1. This can be done by either using a **Bruggeman**, **Tortuosity**, or a **User defined** correlation.

If the **Use Darcy's law for momentum transport** check box has been selected, the **Gas permeability** is defined in this node.

By checking **Include pore-wall interaction**, additional friction forces between the individual gas molecules and the walls are accounted for when computing the gas fluxes (given that **Include gas phase diffusion** is active). The pore-wall friction forces make use of a **Wall diffusivity**, which is set to **Knudsen** by default. The Knudsen diffusivity can be derived from kinetic gas theory by relating the mean-free path of the gas molecules to the **Pore diameter** of the pores.

Gas-Electrolyte Compartment

The **H2 Gas-Electrolyte Compartment** and **O2 Gas-Electrolyte Compartment** nodes specify domains where both an Electrolyte Phase, and a Gas Phase node are active. This node is typically used to model a hydrogen or oxygen evolving electrolyte compartment in a liquid-electrolyte-based electrolyzer.

EFFECTIVE ELECTROLYTE CHARGE TRANSPORT

The bulk electrolyte conductivity defined in the Electrolyte Phase node will be multiplied by a correction factor to compensate for the effect of the **Electrolyte volume fraction** being less than 1 (caused by the evolving gas). This can be done by either using a **Bruggeman**, **Tortuosity**, or **User defined** correlation. For **Tortuosity**, select either **Isotropic** to define a scalar value, or **Diagonal** or **Symmetric** to define anisotropic tensor values.

GAS TRANSPORT

This section will only be visible if the **Include gas phase diffusion** check box or the **Use Darcy's law for momentum transport** check box has been selected in the corresponding **Gas Mixture** section on the interface top node.

If the **Include gas phase diffusion** check box has been selected, the gas diffusivity defined in the Gas Phase node will be multiplied by a correction factor to compensate for the effect of the **Gas pore volume fraction** being less than 1 (caused by the evolving gas). This can be done by either using a **Bruggeman**, **Tortuosity**, or **User defined** correlation. For **Tortuosity**, select either **Isotropic** to define a scalar value, or **Diagonal** or **Symmetric** to define anisotropic tensor values.

If the **Use Darcy's law for momentum transport** check box has been selected, the **Gas permeability** is defined in this node.

Gas Diffusion Electrode

The **H2 Gas Diffusion Electrode** and **O2 Gas Diffusion Electrode** nodes specify three phase domains where an Electronic Conducting Phase, an Electrolyte Phase, and a Gas Phase node are all active.

ELECTRODE CHARGE TRANSPORT

The effective electronic conductivity, **Effective electrical conductivity**, σ_s (SI unit: S/m) parameter will define how the electric current in the corresponding Electronic Conducting Phase domain depends on the gradient of the potential.

EFFECTIVE ELECTROLYTE CHARGE TRANSPORT

The bulk electrolyte conductivity defined in the Electrolyte Phase node will be multiplied by a correction factor to compensate for the effect of the **Electrolyte volume fraction** being less than 1. This can be done by either using a **Bruggeman**, **Tortuosity**, or **User defined** correlation. For **Tortuosity**, select either **Isotropic** to define a scalar value, or **Diagonal** or **Symmetric** to define anisotropic tensor values.

GAS TRANSPORT

This section will only be visible if the **Include gas phase diffusion** check box or the **Use Darcy's law for momentum transport** check box has been selected in the corresponding **Gas Mixture** section on the interface top node.

If the **Include gas phase diffusion** check box has been selected, the gas diffusivity defined in the Gas Phase node will be multiplied by a correction factor to compensate for the effect of the **Gas pore volume fraction** being less than 1. This can be done by either using a **Bruggeman**, **Tortuosity**, or **User defined** correlation. For **Tortuosity**, select either **Isotropic** to define a scalar value, or **Diagonal** or **Symmetric** to define anisotropic tensor values.

If the **Use Darcy's law for momentum transport** check box has been selected, the **Gas permeability** is defined in this node.

By checking **Include pore-wall interaction**, additional friction forces between the individual gas molecules and the walls are accounted for when computing the gas fluxes (given that **Include gas phase diffusion** is active). The pore-wall friction forces make use of a **Wall diffusivity**, which is set to **Knudsen** by default. The Knudsen diffusivity can be derived from kinetic gas theory by relating the mean-free path of the gas molecules to the **Pore diameter** of the pores.

Gas Flow Channel

The **H2 Gas Flow Channel** and **O2 Gas Flow Channel** nodes specify domains with only a Gas Phase node being active.

This node will be available if the **Include gas phase diffusion** check box or the **Use Darcy's law for momentum transport** check box has been selected in the corresponding **Gas Mixture** section on the interface top node.

GAS TRANSPORT

If the **Include gas phase diffusion** check box has been selected, there are no settings on this node. The gas diffusivity defined in the Gas Phase node.

If the **Use Darcy's law for momentum transport** check box has been selected, the **Gas permeability** is defined in this node.

The **Gas permeability** option of **Straight channels** can be used to specify the permeability for a straight channel with a uniform cross section, for which analytical correlations exist for expressing the flow rate as proportional to the volumetric flow. For a rectangular cross section, with height H and width W, the corresponding Darcy permeability κ_g (derived by Boussinesq in 1868) is

$$\kappa_g = \frac{W^2}{12} - \frac{16W^3}{\pi^5 H} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^5} \frac{\cosh(\beta_n H) - 1}{\sinh(\beta_n H)}$$

with β_n being a help variable equal to

$$\beta_n = \frac{(2n-1)\pi}{W}$$

In the COMSOL implementation of the above expression, the sum is truncated to the first ten terms. It should be noted that the analytical expression renders a correct average flow rate for a straight channel with no slip conditions on the channel walls. To resolve the local flow field close to a wall, or for curved channels, solving for the full set of the Navier–Stokes equations (as defined by the **Laminar Flow**, **Brinkman Equations**, or **Free and Porous Media Flow, Brinkman** interfaces) is typically required. However for cases were full accuracy of the local flow field is not required, the above approximation may save substantial computational resources in terms of memory and computation time.

Initial Values

Use this subnode to specify the initial values used by the solver of the dependent variables defined by the parent node.

In the **Initial Values** subnode to the **H2 Gas Phase** and **O2 Gas Phase** nodes, **Mixture specification** in the **Initial Composition** section can be used to specify mixture composition in **Mole fractions** or **Humidified mixture** for all gas phase domains. The **O2 Gas Phase** node has an additional option of **Humidified air** for O2 gas phase domains.

The option **Mole fractions** is always available and text fields are used to specify the mixture composition for all included species.

Humidified mixture allows for specifying a gas mixture using values for a dry gas mixture, which is subsequently humidified to a specified relative humidity. The setting is available if H2O has been selected in the corresponding **Gas Mixture** section on the interface top node, and text fields are used to specify the mixture composition for all included species except H2O. Additionally, the **Relative humidity**, **Humidification temperature**, and **Humidification absolute pressure** of the humidifier are also specified.

Humidified air is available if H2O and N2 have been selected in the **O2 Gas Mixture** section on the interface top node. **Relative humidity**, **Humidification temperature**, and **Humidification absolute pressure** of the humidifier are also specified. The dry mole fractions of the included species are set internally as follows: 0.79 (N2), 4e-4 (CO2) and 1e-6(CO).

Given that the humidifier (inlet) temperature (T_{hum}), absolute pressure ($p_{A,hum}$) and relative humidity (RH_{hum}) of the humidifier (inlet) gases are known, the conversion from a set of dry (containing no water vapor) molar fraction to a corresponding humidified mixture may be calculated as follows. The water mole fraction is defined as

$$x_{H2O} = \frac{p_{vap}(T_{hum})}{p_{A,\,hum}}RH_{hum}$$

The wet mole fractions for all species except water are then calculated from the dry mixture molar fractions according to

$$x_i = x_{i,\,dry}(1 - x_{H2O})$$

In the **Initial Values** subnode to the **Membrane** node, **Specify water chemical potential as** can be used to specify water **Activity**, **Liquid water pressure**, or water **Chemical potential**. The default **From parent** option specifies water activity for **Vapor equilibrated** model and liquid water pressure for **Liquid equilibrated** model, respectively, chosen on the parent node.

Initial Values, O2 Domains

Use this subnode to specify the initial values used by the solver of the dependent variables defined by the parent Electronic Conducting Phase node.

The selection is locked to the intersection of the parent node and the O2 Gas Phase node.

Initial Values, H2 Domains

Use this subnode to specify the initial values used by the solver of the dependent variables defined by the parent Electronic Conducting Phase node.

The selection is locked to the intersection of the parent node and the H2 Gas Phase node.

Water Condensation-Evaporation

This subnode is available to the Gas Phase nodes when H2O has been selected, along with **Include gas phase diffusion** or **Use Darcy's law for momentum transport** in the corresponding **Gas Mixture** section on the interface top node.

In low-temperature fuel cells or electrolyzers, gaseous water vapor may condensate as liquid water if the partial pressure of vapor exceeds the (equilibrium) vapor pressure as follows

$$H_2O(g) \leftrightarrow H_2O(l)$$
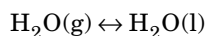
The node may be used for adding an additional mass source due to water condensation-evaporation. Note that mass source may also be added to liquid water if **Include H2O(l) in reaction stoichiometry** is active in the corresponding **Gas Mixture** section on the interface top node. The **Condensation-Evaporation Rate** may be defined using the **From vapor pressure**, or by a **User defined** expression. The node contains text fields for specifying the **Rate constant** and **Reference pressure**, in case of the default **From vapor pressure** option. The rate expression is added to the rate variable for gaseous water (based on the reaction stoichiometry), which is in turn used in the domain equations for diffusion and/or Darcy's law if these are active on the interface top node.

The **Heat of reaction** is calculated automatically when the **Built in** option is used.

The default selection is all domains of the parent node, but may be changed.

Water Gas Shift Reaction

This subnode is available to the H2 Gas Phase node when H2O, CO, and CO2 have all been selected, along with **Include gas phase diffusion** in the **H2 Gas Mixture** on the interface top node.

The water gas shift reaction defines the reaction of carbon monoxide and water vapor to form carbon dioxide and hydrogen according to

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g)$$
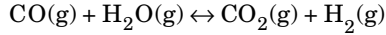
The water gas shift reaction is of particular interest for fuel cells operating on fuel stemming from hydrocarbon reformation, containing significant amounts of carbon dioxide and carbon monoxide. The reaction is also of general interest in molten carbonate fuel cells and electrolyzers, due to the presence of carbon dioxide in the hydrogen fuel/product fluid stream.

The node may be used for adding an additional mass source due to water gas shift reaction, such as in a molten carbonate fuel cell. The **Water Gas Shift Reaction Rate** may be defined using the **From mass action law** or by a **User defined** expression. The node contains text fields for specifying the **Rate constant** and **Reference pressure**, in case of the default **From mass action law** option. The rate expression is added to the rate variables for the gaseous species (based on the reaction stoichiometry), which are in turn used in the domain equations for diffusion. Since the reaction does not involve phase changes, the total mass source from the water gas shift reaction is zero, and no contribution is hence made to the momentum equation.

The **Heat of reaction** is calculated automatically when the **Built in** option is used.

The default selection is all domains of the parent node, but may be changed.

Reaction Sources

This subnode is available to the Gas Phase nodes when the **Advanced Physics Options** is selected in the **Show More Options** dialog box shown when the **Show More Options** button (☞) is selected, in combination with the **Include gas phase diffusion** or **Use Darcy's law for momentum transport** check box being selected in the interface top node for the corresponding gas mixture.

The node may be used for adding additional mass sources in a model, typical stemming from nonfaradaic reactions such as water condensation-evaporation or water drag in a low-temperature fuel cell, or homogeneous reactions such as the water gas shift reaction in a molten carbonate fuel cell. The node contains text fields for specifying the reaction sources of all active gas phase species, including liquid water.

The default selection is all domains of the parent node, but may be changed.

Gas Diffusion Electrode Reaction

The **H2 Gas Diffusion Electrode Reaction** and **O2 Gas Diffusion Electrode Reaction** are available as subnodes to the corresponding Gas Diffusion Electrode parent nodes.

The node specifies the stoichiometry, thermodynamics, and kinetics of a gas diffusion electrode reaction.

STOICHIOMETRIC COEFFICIENTS

Specify the coefficients using negative signs for oxidized species and positive signs for reduced species. The number of electrons should always be positive.

EQUILIBRIUM POTENTIAL

The equilibrium potential may be defined using the **Nernst equation**, **From material**, or by a **User defined** expression.

The **Built in** option for the **Reference equilibrium potential** is based on the reaction stoichiometry and the enthalpies and entropies of the reacting species.

See also Calculation of Built-in Equilibrium and Thermoneutral Potentials and Electrode Reaction in Shared Physics Features in the Current Distribution Interfaces.

REFERENCE PRESSURES

Both the exchange current density and the equilibrium potential of an electrode reaction depend on the partial pressures of the reacting species. By the use of a reference state (a given set of partial pressures) and the **Reference equilibrium potential** and **Reference exchange current density**, analytical expressions such as the **Nernst equation** (for the equilibrium potential) and **Mass action law** or **Lumped multistep** (for the **Butler–Volmer** kinetics) may be used to calculate the corresponding partial-pressure dependent values.

Specify the species partial pressures for the reference state used for defining the **Reference exchange current density** and the **Reference equilibrium potential**. The default value (1 atm) refers to standard conditions.

If the **Reference equilibrium potential** is set to **Built in**, the settings of this section only applies to the **Reference exchange current density**.

ELECTRODE KINETICS

The settings of this section define how the overpotential of the electrode reaction relates to the local current density on the (catalyst) electrode surface.

See also Electrode Reaction in Shared Physics Features in the Current Distribution Interfaces.

ACTIVE SPECIFIC SURFACE AREA

Specify the active surface (catalyst) area available for the reaction.

HEAT OF REACTION

The settings of this section define the heat source of the reaction.

The **Built in** option for the **Thermoneutral voltage** is based on the reaction stoichiometry and the entropies of the reacting species.

See also Calculation of Built-in Equilibrium and Thermoneutral Potentials and Electrode Reaction in Shared Physics Features in the Current Distribution Interfaces.

Porous Double Layer Capacitance

See Porous Matrix Double-Layer Capacitance in Shared Physics Features in the Current Distribution Interfaces.

Overview of the Boundary Nodes in the Hydrogen Fuel Cell and Water Electrolyzer Interfaces

Boundary nodes applying constraints or flux contributions to one phase only are added as subnodes. The following boundary subnodes may be added to Electronic Conducting Phase:

- Insulation (default)
- Electric Ground
- Electric Potential
- Electrode Current
- Electrode Current Density
- Electrode Power
- Internal Electrode Contact Resistance

The following boundary subnodes may be added to Electrolyte Phase:

- Insulation (default)
- Electrolyte Potential

- Electrolyte Current Density
- Internal Electrolyte Contact Resistance

The following boundary subnodes may be added to H2 or O2 Gas Phase:

- No Flux (default)
- Inlet
- Outlet
- Flux

The following boundary subnodes may be added to Membrane:

- Water Absorption-Desorption, H2/O2 side (default)
- Water Flux
- Water Chemical Potential

The following additional boundary nodes, with contributions to multiple phases, can be added as nodes directly under the interface node:

- Thin Gas Diffusion Electrode
- Electrode Surface
- Internal Electrode Surface

Insulation

The **Insulation** boundary condition describes the walls of a cell or the boundaries of the cell that do not face a conductor. The boundary condition imposes the following equation:

$$\mathbf{i}_k \cdot \mathbf{n} = 0$$

where $\mathbf{i}_k$ denotes the current density vector and $k = l, s$ is an index for the electrolyte and electrode, respectively.

The node can be added as a subnode to either Electrolyte Phase or Electronic Conducting Phase.

Electrolyte Potential

Add the **Electrolyte Potential** node as a subnode to the Electrolyte Phase for a boundary with a fixed potential at a position in the electrolyte.

The node sets the potential in the electrolyte, ϕ_l, to be equal to the **Boundary electrolyte potential**, $\phi_{l,\text{bnd}}$ (SI unit: V).

Electrolyte Current Density

Use the **Electrolyte Current Density** node as a subnode to the Electrolyte Phase to specify the current density distribution along a boundary.

Note that using this node in 2D or 3D may result in an uneven potential distribution along the boundary.

Internal Electrolyte Contact Resistance

Use the **Internal Electrolyte Contact Resistance** node as a subnode to the Electrolyte Phase to specify a **Contact resistance** at an internal boundary of the domain selection of the Electrolyte Phase. The contact resistance is modeled by adding slit boundary conditions. The slit boundary defines separate degrees of freedom for the electrolyte potential at the up and down sides of the slit boundary, and then adds current density (Neumann) conditions at both the up and down side.

Electric Ground

The node can be added as a subnode to Electronic Conducting Phase. This node sets the electric potential to zero. The node is typically used to ground the voltage at the current collector of the hydrogen side of the cell.

CONTACT RESISTANCE

Enabling **Include contact resistance** allows for a **Contact resistance** R_c (SI unit: $\Omega \cdot \text{m}^2$) to be specified and the following current density condition is used:

$$-\mathbf{n} \cdot \mathbf{i}_s = \frac{-\phi_s}{R_c}$$

Electric Potential

The node can be added as a subnode to Electronic Conducting Phase. This node sets the electric potential in the electrode (or a porous electrode), ϕ_s, to a value, $\phi_{s,\text{bnd}}$ according to the following:

$$\phi_s = \phi_{s,\text{bnd}}$$

The node is typically used to set the cell voltage at the current collector of the oxygen side of the cell.

CONTACT RESISTANCE

Enabling **Include contact resistance** allows for a **Contact resistance** R_c (SI unit: $\Omega \cdot m^2$) to be specified and the following current density condition is used:

$$-\mathbf{n} \cdot \mathbf{i}_s = \frac{\phi_{s,\,bnd} - \phi_s}{R_c}$$

HARMONIC PERTURBATION

Enable **Include harmonic perturbation** to specify the **Perturbation amplitude** value. This setting will be used by the **Frequency-Domain Perturbation** study step when running an **AC Impedance study**.

Electrode Current

Use the **Electrode Current** node to set the total current or average current density over an external at an external boundary of an Electronic Conducting Phase domain — typically at the interface between the electrode and the current collector or current feeder. The condition sets the total inward current without imposing the current density distribution. The potential along the boundary is calculated in order to satisfy the total value of the current.

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) parameters.

CONTACT RESISTANCE

Enabling **Include contact resistance** allows for a **Contact resistance** R_c (SI unit: $\Omega \cdot m^2$) to be specified.

HARMONIC PERTURBATION

Enable **Include harmonic perturbation** to specify the **Perturbation amplitude** value. This setting will be used by the **Frequency-Domain Perturbation** study step when running an **AC Impedance study**.

Electrode Current Density

The **Electrode Current Density** boundary condition can be added as a subnode to and applied at an external boundary of an Electronic Conducting Phase domain.

Note that using this node in 2D or 3D may result in an uneven potential distribution along the boundary. To mitigate such effects, use the Electrode Current node instead.

HARMONIC PERTURBATION

Enable **Include harmonic perturbation** to specify the **Perturbation amplitude** value. This setting will be used by the **Frequency-Domain Perturbation** study step when running an **AC Impedance study**.

Electrode Power

The **Electrode Power** boundary condition sets the power drawn from, or inserted to, the cell at an external boundary of an Electronic Conducting Phase domain

When using the **Total power** option in 1D or 2D, the boundary area is based either on the **Cross-sectional area** (1D), or the **Out-of-Plane thickness** (2D) parameters.

CONTACT RESISTANCE

Enabling **Include contact resistance** allows for a **Contact resistance** R_c (SI unit: $\Omega \cdot m^2$) to be specified.

Internal Electrode Contact Resistance

Use the **Internal Electrode Contact Resistance** node as a subnode to the Electronic Conducting Phase to specify a **Contact resistance** at an internal boundary of the domain selection of the Electronic Conducting Phase. The contact resistance is modeled by adding slit boundary conditions. The slit boundary defines separate degrees of freedom for the electric potential at the up and down sides of the slit boundary, and then adds current density (Neumann) conditions at both the up and down side.

No Flux

The **No Flux** node is the default boundary condition available for exterior boundaries of Gas Phase nodes. 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.

Inlet

The **H2 Inlet** and **O2 Inlet** nodes adds a boundary condition for an inflow boundary, defining the composition of the mixture and the flow boundary condition.

This node is available for exterior boundaries to Gas Phase nodes.

The **Mixture specification** section is available if the **Include gas phase diffusion** check box has been selected on the interface top node. The mixture composition can be specified using the following quantities in:

- **From initial values** (default)
- **Mole fractions**: $x_i = x_{0,i}$
- **Humidified mixture**
- **Humidified air**
- **Mass fractions**: $\omega_i = \omega_{0,i}$
- **Mole fractions**: $x_i = x_{0,i}$
- **Molar concentrations**: $c_i = c_{0,i}$
- **Number densities**, which describes the number of particles per volume: $n_i = n_{0,i}$
- **Densities**: $\rho_i = \rho_{0,i}$
- **Mass flow rates**: $J_{0,i}$

The section requires input for all selected gas species.

Humidified mixture allows for specifying a gas mixture using values for a dry gas mixture, which is subsequently humidified to a specified relative humidity. The setting is available if H2O has been selected in the corresponding **Gas Mixture** section on the interface top node, and text fields are used to specify the mixture composition for all included species except H2O. Additionally, the **Relative humidity**, **Humidification temperature**, and **Humidification absolute pressure** of the inlet humidifier are also specified.

Humidified air is available for the **O2 Inlet** node, if H2O and N2 have been selected in the **O2 Gas Mixture** section on the interface top node. **Relative humidity**, **Humidification temperature**, and **Humidification absolute pressure** of the inlet humidifier are also specified. The dry mole fractions of the included species are set internally as follows: 0.79 (N2), 4e-4 (CO2) and 1e-6(CO).

Given that the humidifier (inlet) temperature (T_{hum}), absolute pressure ($p_{A,hum}$) and relative humidity (RH_{hum}) of the humidifier (inlet) gases are known, the conversion

from a set of dry (containing no water vapor) molar fraction to a corresponding humidified mixture may be calculated as follows. The water mole fraction is defined as

$$x_{\text{H2O}} = \frac{p_{\text{vap}}(T_{\text{hum}})}{p_{A,\text{hum}}}\text{RH}_{\text{hum}}$$

The wet mole fractions for all species except water are then calculated from the dry mixture molar fractions according to

$$x_i = x_{i,\text{dry}}(1 - x_{\text{H2O}})$$

The **Flow boundary condition** section is available if the **Use Darcy's law for momentum transport** check box has been selected on the interface top node. The flow inlet condition can be specified using **From initial values**, **Pressure**, or **Total mass flow rate** options.

Outlet

The **H2 Outlet** and **O2 Outlet** nodes are the preferred boundary conditions at outlets where the species are to be transported out of the model domain. It is useful at outlets where it is assumed that convection is the dominating effect driving the mass flow.

This node is available for exterior boundaries to Gas Phase nodes.

If the **Include gas phase diffusion** check box has been selected on the interface top node, the boundary condition is applied to all selected gas species and corresponds to:

$$-\mathbf{n} \cdot \rho\omega_i \sum_k D_{ik}\mathbf{d}_k = 0$$

If the **Use Darcy's law for momentum transport** check box has been selected on the interface top node, the outlet **Pressure** can be specified.

Flux

This subnode is available to the Gas Phase nodes when the **Advanced Physics Options** is selected in the **Show More Options** dialog box shown when the **Show More Options** button (☞) is selected, in combination with the **Include gas phase diffusion** or **Use Darcy's law for momentum transport** check box being selected in the interface top node for the corresponding gas mixture.

The node may be used for adding additional boundary mass fluxes in a model, typical stemming from nonfaradaic reactions such as water condensation-evaporation on a channel wall or diffusion of gaseous species into adjacent media. The node contains text fields for specifying the inward mass fluxes of all active gas phase species.

This node is available for exterior boundaries to Gas Phase nodes.

Water Absorption-Desorption

The **Water Absorption-Desorption, H2 side** and **Water Absorption-Desorption, O2 side** nodes are available if **Electroosmotic water drag** has been selected in the **Membrane Transport** section on the interface top node. These nodes are added by default and the selection is locked to all intersection boundaries of the Membrane and the respective Gas Phase nodes.

The node sets up the boundary conditions that define the absorption-desorption water flux between the membrane and the neighboring gas phase domain. The node also contributes to the boundary heat source variable, based on the **Heat of water absorption** parameter on the parent node.

The **Absorption-Desorption Condition** can be specified as **Vapor absorption-desorption** (by specifying an **Absorption-desorption rate constant**), **Liquid water pressure**, water **Chemical potential**, or **User-defined rate**. The default **From parent** option is identical to the **Vapor absorption-desorption** option for **Vapor equilibrated** model and **Liquid water pressure** option **Liquid equilibrated** model, respectively, chosen on the parent node.

The **Water absorbs-desorbs as** setting controls if the node should contribute to the rate variables for gaseous or liquid water. This setting is available for **Chemical potential** or **User-defined rate** options. If **Gas** is selected, and if the **Include gas phase diffusion** check box or the **Use Darcy's law for momentum transport** check box has been selected in the corresponding **Gas Mixture** section on the interface top node, the corresponding absorption-desorption mass fluxes are added to these equations. If **Liquid** is selected, the corresponding absorption-desorption mass flux is added to the flux variable for $H2O(l)$, if **Include H2O(l) in reaction stoichiometry** is active in the corresponding **Gas Mixture** section on the interface top node. Note that **Vapor absorption-desorption** will absorb-desorb water as for the **Gas** setting and **Liquid water pressure** as for the **Liquid** setting.

Water Flux

This subnode is available to the Membrane node when the **Advanced Physics Options** is selected in the **Show More Options** dialog box shown when the **Show More Options** button (👁) is selected, in combination with the **Electroosmotic water drag** being selected in the **Membrane Transport** section on the interface top node.

This node is available for exterior boundaries to Membrane node.

Water Chemical Potential

This subnode is available to the Membrane node when the **Advanced Physics Options** is selected in the **Show More Options** dialog box shown when the **Show More Options** button (👁) is selected, in combination with the **Electroosmotic water drag** being selected in the **Membrane Transport** section on the interface top node.

This node is available for exterior boundaries to Membrane node.

Thin Gas Diffusion Electrode

Use the **Thin H2 Gas Diffusion Electrode** or the **Thin O2 Gas Diffusion Electrode** nodes to define a thin gas diffusion electrode located at a boundary between an Electrolyte Phase, an Electronic Conducting Phase and a Gas Phase node.

The electrode is assumed to be so thin that any current and species distribution effects along the electrode thickness can be neglected.

The volumetric current density and corresponding mass sources/fluxes of the Thin Gas Diffusion Electrode Reaction subnodes are multiplied by the **Electrode Thickness** parameter, and applied as a boundary conditions.

FILM RESISTANCE

Use a film resistance if you want to include an additional potential drop due to an ohmic resistance at the interface between the electrode and the electrolyte (a contact resistance), for instance due to build-up of insulating deposits.

Specify either a **Surface resistance** R_{film} (SI unit: $\Omega \cdot \mathrm{m}^2$) directly or choose the **Thickness and conductivity** option to calculate the surface resistivity based on a depositing film thickness.

Electrode Surface

Use the **H2 Electrode Surface** or the **O2 Electrode Surface** nodes to define an electrode surface located at external boundaries of a H2/O2 Gas-Electrolyte Compartment domain that are also external to the domain selection of the interface. Set the electric potential of the electrode or specify a current condition that the potential of the electrode shall fulfill.

FILM RESISTANCE

Use a film resistance if you want to include an additional potential drop due to an ohmic resistance at the interface between the electrode and the electrolyte (a contact resistance), for instance due to build-up of insulating deposits.

Specify either a **Surface resistance** R_{film} (SI unit: $\Omega \cdot m^2$) directly or choose the **Thickness and conductivity** option to calculate the surface resistivity based on a depositing film thickness.

Specify the electrode reaction using Electrode Reaction child nodes.

Internal Electrode Surface

Use the **Internal H2 Electrode Surface** or the **Internal O2 Electrode Surface** nodes to define an internal electrode surface located at boundaries adjacent to both an external boundary of a H2/O2 Gas-Electrolyte Compartment domain and an external boundary of an Electronic Conducting Phase domain.

FILM RESISTANCE

Use a film resistance if you want to include an additional potential drop due to an ohmic resistance at the interface between the electrode and the electrolyte (a contact resistance), for instance due to build-up of insulating deposits.

Specify either a **Surface resistance** R_{film} (SI unit: $\Omega \cdot m^2$) directly or choose the **Thickness and conductivity** option to calculate the surface resistivity based on a depositing film thickness.

Specify the electrode reaction using Electrode Reaction child nodes.

Thin Gas Diffusion Electrode Reaction

This node can be added as a subnode to a Thin Gas Diffusion Electrode node.

Regarding the settings of the node, see Gas Diffusion Electrode Reaction.

Electrode Reaction

This node can be added as a subnode to Electrode Surface and Internal Electrode Surface nodes.

Regarding the settings of the node, see Gas Diffusion Electrode Reaction.

Theory for the Hydrogen Fuel Cell and Water Electrolyzer Interfaces

In this chapter:

- Electronic Conducting Phase Theory
- Electrolyte Phase Theory
- Gas Phase Theory
- Calculation of Built-in Equilibrium and Thermoneutral Potentials
- Membrane Crossover Theory
- Electroosmotic Water Drag Theory

For general theory on electrode reactions, kinetics, as well as mass and heat sources, see also

- Electrode Kinetics Expressions
- Equilibrium Potentials and the Nernst Equation
- Mass Fluxes and Sources Due to Electrochemical Reactions
- Joule Heating Due to Charge Transport
- Heating Due to Electrochemical Reactions

in Theory for the Current Distribution Interfaces.

For general theory on thermodynamic models, see also

- Thermodynamic Models and Theory

Electronic Conducting Phase Theory

The Electronic Conducting Phase node solves for the electric potential ϕ_s (V) as dependent variable.

The current density in the phase, $\mathbf{i}_s$ (A/m^2), is defined as (Ref. 1)

$$\mathbf{i}_s = -\sigma_{s,\,\text{eff}} \nabla \phi_s \qquad (3\text{-}1)$$

where $\sigma_{s,\,\text{eff}}$ is the effective electric conductivity (S/m).

The charge balance equation in the phase is defined as

$$\nabla \cdot \mathbf{i}_s = -i_{v, \text{tot}} \tag{3-2}$$

where $i_{v,\text{tot}}$ (A/m^3) is the sum of a volumetric current density contributions of the electrode reactions occurring in the Gas Diffusion Electrode domains.

For Current Collector and Gas Diffusion Layer domains,

$$\nabla \cdot \mathbf{i}_s = 0$$

Electrolyte Phase Theory

The Electrolyte Phase node solves for the electric potential ϕ_l (V) as dependent variable.

The current density in the phase, $\mathbf{i}_l$ (A/m^2), is defined as (Ref. 1)

$$\mathbf{i}_l = -\sigma_{l, \text{eff}} \nabla \phi_l \tag{3-3}$$

where $\sigma_{l, \text{eff}}$ is the effective electrolyte conductivity (S/m).

The charge balance equation in the phase is defined as

$$\nabla \cdot \mathbf{i}_l = i_{v, \text{tot}} \tag{3-4}$$

where $i_{v,\text{tot}}$ (A/m^3) is the sum of a volumetric current density contributions of the electrode reactions occurring in the Gas Diffusion Electrode domains.

For Membrane, Separator and Gas-Electrolyte Compartment domains

$$\nabla \cdot \mathbf{i}_l = 0$$

Gas Phase Theory

GAS PHASE DIFFUSION

When gas phase diffusion is enabled, the gas phase nodes solve for a set of mass fraction variables, ω_i, where i is the index of the species. The governing equations are defined using the Maxwell–Stefan set of equations, as described in Theory for the Transport of Concentrated Species Interface.

DARCY'S LAW

When Darcy's law is enabled, the gas phase nodes solve for a pressure variable p (Pa).

The Darcy's law equations are documented in Theory for the Darcy's Law Interface.

BUILT-IN BINARY DIFFUSION COEFFICIENTS

The calculation of the built-in binary diffusion coefficients is done using the Fuller–Schettler–Giddings (FGS) model (Ref. 2):

$$D_{i,j}^0 = \frac{1.01325 \times 10^{-2} T^{1.75} \sqrt{\frac{1}{M_i} + \frac{1}{M_j}}}{P\left(\left(\sum_i v\right)^{\frac{1}{3}} + \left(\sum_j v\right)^{\frac{1}{3}}\right)^2} \tag{3-5}$$

where T denotes the temperature (K), M_i the molecular weight of species i (g/mol), P is the pressure (Pa), and v_i are the atomic diffusion volumes (Fuller diffusion volume) (cm^3).

TABLE 3-1: DIFFUSION VOLUMES USED FOR CALCULATING BINARY DIFFUSION COEFFICIENTS.

SPECIES	FULLER DIFFUSION VOLUME
H_2	6.12
O_2	16.3
H_2O	13.1
N_2	18.5
CO	18
CO_2	26.9
CH_4	25.15

BUILT-IN DYNAMIC VISCOSITY

The built-in mixture viscosity of the gas phase is based on kinetic theory by Brokaw (Ref. 3):

$$\eta_v = \sum_i \left(\frac{x_i \eta_{i,v}}{\sum_j x_j \psi_{i,j}}\right)$$

where

$$\psi_{i,j} = A_{i,j}\sqrt{\frac{\eta_{i,v}}{\eta_{j,v}}} \tag{3-6}$$

and the interaction parameter is defined as

$$A_{i,j} = \frac{\beta_{i,j}}{\sqrt{RM_{i,j}}}\left(1 + \frac{RM_{i,j} - RM_{i,j}^{0.45}}{2(1 + RM_{i,j}) + \frac{1 + RM_{i,j}^{0.45}}{(\sqrt{\beta_{i,j}})(1 + RM_{i,j})}}\right) \tag{3-7}$$

with

$$\beta_{i,j} = \left(\frac{4M_iM_j}{(M_i + M_j)^2}\right)^{1/4}, \quad RM_{i,j} = \frac{M_i}{M_j} \tag{3-8}$$

where $\eta_{i,v}$ is the vapor viscosity of each individual species, and M_i are the molecular weights.

BUILT-IN THERMAL CONDUCTIVITY

The gas phase mixture thermal conductivity, which may be used in heat transfer simulations, is calculated by the Hydrogen Fuel Cell and Water Electrolyzer interfaces according to (Ref. 4)

$$\lambda_v = \sum_i \left(\frac{x_i\lambda_{i,v}}{\sum_j x_j\phi_{i,j}}\right) \tag{3-9}$$

$$\phi_{i,j} = \frac{1}{4}\left(1 + \sqrt{\frac{\eta_{i,v}}{\eta_{j,v}}\left(\frac{M_j}{M_i}\right)^{3/4}\left(\frac{T + \left(\frac{3}{2}\right)T_{b,i}}{T + \left(\frac{3}{2}\right)T_{b,j}}\right)}\right)^2 \left(\frac{T + S_{ij}\sqrt{\left(\frac{9}{4}\right)T_{b,i}T_{b,j}}}{T + \left(\frac{3}{2}\right)T_{b,i}}\right) \tag{3-10}$$

In the above formula, the summations are done for all active species, where $\lambda_{i,v}$ and $\eta_{i,v}$ are the individual vapor thermal conductivity and dynamic viscosity correlations as a functions of temperature for the pure gases, respectively. The normal boiling points $T_{b,i}$ and the species molecular weights are also considered. The factor S_{ij} equals 0.773 if either i or j represents the index of water (steam). For all other cases $S_{ij} = 1$.

Since the above equation relies on the individual species viscosities, the thermal conductivity is only calculated in gas phase domains using built-in (that is, not user-defined) dynamic viscosities.

BUILT-IN HEAT CAPACITY

The Hydrogen Fuel Cell and Water Electrolyzer interfaces also calculate the heat capacity of the gas mixture which may be used in heat transfer simulations. The heat capacity is calculated as

$$C_{p,\,\mathrm{mix}} = \sum_i \frac{\omega_i c_{p,i}}{M_i}$$

where $C_{p,\mathrm{mix}}$ is the heat capacity of the fluid mixture in J/(kg·K), $c_{p,i}$ is the species heat capacity in J/(mol·K).

Calculation of Built-in Equilibrium and Thermoneutral Potentials

The change of enthalpy for an electrode reaction is (Ref. 1)

$$\Delta_r H = \sum_i \upsilon_i H_i$$

where $H_i = H_i(T)$ are the enthalpies of formation of the reacting species of index i, and υ_i the stoichiometric coefficients.

Similarly, the change of entropy is

$$\Delta_r S = \sum_i \upsilon_i S_i$$

Where $S_i = S_i(T)$ is the (absolute) molar entropy.

H_i and S_i are generally known for liquids and gases, whereas for ions the values will depend on the nature of the electrolyte in use, and are hence hard to measure experimentally.

The corresponding change of Gibbs free energy of a reaction is

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

The equilibrium potential for an electrode reaction is

$$E_{eq} = \frac{-\Delta_r G}{nF}$$

and the thermoneutral voltage, required to compute electrode reaction heat sources, is

$$E_{therm} = \frac{-\Delta_r H}{nF}$$

where n is the number of electrons included in the electrode reaction.

Temperature dependent thermodynamic expressions for gaseous species of $H_i(T)$ and $S_i(T)$, at standard partial pressures of 1 atm, are based on Ref. 6.

For the charge-conducting ion in the electrolyte, entropy, and enthalpy values are however generally not known and need to be set by the user. The stoichiometric coefficient of the charge-carrying ion is derived from the number of electrons participating in the charge transfer reaction and the charge carrying ion charge as

$$\nu_{ion} = -\frac{n}{z_{ion}}$$

For convenience, the built-in equilibrium potentials are defined versus a reversible reference hydrogen electrode (RHE) for the same electrolyte type, for a specified reference temperature. This will have the effect that the HOR/HER will have an equilibrium potential in a model close to 0 V, and the ORR/OER reaction will have an equilibrium potential ranging from around 1.2 (at room temperature) to 1.0 V (at 800°C). This shift facilitates setting for instance initial values for the potential dependent variables in a model.

The reference equilibrium and thermoneutral potentials used by the electrode reaction node, versus the RHE, are defined as

$$E_{eq, ref} = \frac{-\Delta_r G_{ref}}{nF} - E_{eq, RHE}$$

and

$$E_{therm} = \frac{-\Delta_r H}{nF} - E_{eq, RHE}$$

where

$$\Delta_r G_{ref} = \Delta_r H - T\Delta_r S_{ref}$$

with ΔS_{ref} being the change in entropy at the chosen reference conditions (typically 1 atm).

Note that due to cancellation in the equation for $E_{\mathrm{eq,\,ref}}$, the values of the ion entropy (0 by default) has no impact on the equilibrium potentials values (nor the overall cell voltage and energy balance), but it will impact how the thermoneutral voltage E_{therm} and corresponding heat sources for the individual electrode reactions are computed.

LIQUID WATER THERMODYNAMIC EXPRESSIONS AND RELATIVE HUMIDITY

The fc/we interface defines the water vapor pressure, p_{vap} (Pa), and the enthalpy of vaporization H_{vap} (J/mol), by the use of an experimental correlations (interpolation) functions vs temperature. The $p_{\mathrm{vap}}(T)$ correlation is based on Ref. 5, whereas $H_{\mathrm{vap}}(T)$ is defined using the same source data as in the Thermodynamics node (See Using Thermodynamic Properties).

The enthalpy of formation of liquid water, $H_{\mathrm{H2O(l)}}$ (J/mol), is then defined as

$$H_{\mathrm{H2O(l)}} = H_{\mathrm{H2O(g)}} - H_{\mathrm{vap}}$$

Assuming that the vapor behaves as an ideal gas, and that the liquid water is incompressible, the following equation for the entropy of liquid water can be derived

$$S_{\mathrm{H2O(l)}} = -R\ln\frac{p_{\mathrm{vap}}}{p_{\mathrm{ref}}} - \frac{H_{\mathrm{vap}}}{T} + S_{\mathrm{H2O(g)}}$$

The relative humidity, RH (1), is defined as

$$\mathrm{RH} = \frac{p_{\mathrm{vap}}}{p_{\mathrm{ref}}}$$

Membrane Crossover Theory

In a membrane-based fuel cell or electrolyzer, the reacting gases may dissolve into the membrane and diffuse through the membrane to the other side of the cell. This cross-membrane transport of species is termed crossover.

For hydrogen and oxygen, these species will be quickly oxidized/reduced when reaching the other side of the cell. These reactions give rise to small parasitic current densities which will have an effect on, for instance, the open circuit voltage of the cell. For nitrogen, typically diffusing from the oxygen to the hydrogen side in air-operated fuel cells, the crossover may result in a dilution effect of the hydrogen fuel.

HYDROGEN CROSSOVER REACTIONS

On the hydrogen side of the membrane, hydrogen dissolves into the membrane according to

$$H_2(g) \leftrightarrow H_2(mem)$$
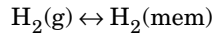
The dissolved hydrogen then diffuses through the membrane, and in the gas diffusion electrode on oxygen side, the hydrogen gets oxidized according to (depending on charge-carrying ion):

Proton exchange:

$$H_2(mem) \rightarrow 2H^+ + 2e^-$$
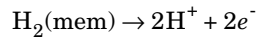
Hydroxide exchange:

$$H_2(mem) + 2OH^- \rightarrow 2H_2O(g) + 2e^-$$
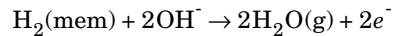
Due to the highly anodic overpotential potential for the hydrogen oxidation reaction on the oxygen side, the reaction operates at a limiting current density, completely governed by the molar flux of hydrogen though the membrane.

OXYGEN CROSSOVER REACTIONS

Similarly as for hydrogen, on the oxygen side of the membrane, oxygen dissolves into the membrane according to

$$O_2(g) \leftrightarrow O_2(mem)$$
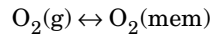
The dissolved oxygen then diffuses through the membrane and in the gas diffusion electrode on hydrogen side, oxygen gets reduced according to (depending on the charge-carrying ion):

Proton exchange:

$$O_2(mem) + 4H^+ + 4e^- \leftrightarrow 2H_2O(g)$$

Hydroxide exchange:

$$O_2(mem) + 2H_2O(g) + 4e^- \leftrightarrow 4OH^-$$
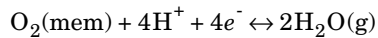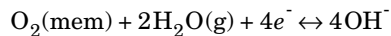
Due to the highly cathodic overpotential potential for the oxygen reduction reaction on the hydrogen side, the reaction operates at a limiting current density, completely governed by the molar flux of oxygen though the membrane.

NITROGEN CROSSOVER REACTIONS

On either side of the membrane, nitrogen may dissolve into and out of the membrane according to

$$N_2(g) \leftrightarrow N_2(mem)$$
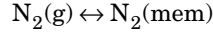
MEMBRANE CROSSOVER TRANSPORT MODEL

The membrane crossover model defines either one or several thermodynamical activities of hydrogen and oxygen in the membrane, a_{H2}, a_{O2}, and a_{N2}, respectively, as dependent variables. The governing equation for the membrane species is based on Fick's law of diffusion in combination with Henry's law

$$\frac{\partial c_{i,\,\mathrm{mem}}}{\partial t} + \nabla \cdot \mathbf{J}_{i,\,\mathrm{mem}} = 0$$

$$\mathbf{J}_{i,\,\mathrm{mem}} = -\Psi_i p_{\mathrm{ref}} \nabla a_i$$

where $\mathbf{J}_{i,\mathrm{mem}}$ (mol/(m^2·s)) is the molar flux of the species and Ψ_i (mol/(m·s Pa)) is the corresponding permeation coefficient. p_{ref} is a reference pressure, arbitrarily set to 1 atm.

The species concentration in the membrane $c_{i,\mathrm{mem}}$ (mol/m^3) used in the time derivative term is calculated based on Henry's law according to

$$c_{i,\,\mathrm{mem}} = a_i \frac{p_{\mathrm{ref}}}{RT} H_i$$

where H_i (1) is the Henry's law coefficient of the species.

Note that, for isothermal conditions, the transport equation is equivalent to Fick's law of diffusion according to

$$\frac{\partial c_{i,\,\mathrm{mem}}}{\partial t} + \nabla \cdot (-D_i \nabla c_{i,\,\mathrm{mem}}) = 0$$

with the diffusion coefficient D_i (m^2/s) defined as

$$D_i = \frac{\Psi_i RT}{H_i}$$

Hydrogen boundary conditions:

On Membrane boundaries adjacent to hydrogen Gas Phase domains, the hydrogen activity a_{H2} is set as follows

$$a_{H2} = \frac{p_{H2(g)}}{p_{ref}}$$

where $p_{H2(g)}$ is the hydrogen partial pressure in the adjacent gas phase. Hydrogen is assumed to be instantly oxidized when it reaches an electrode on the oxygen gas side. On Membrane boundaries adjacent to oxygen Gas Diffusion Electrode domains (or oxygen Thin Gas Diffusion Electrode boundaries), the hydrogen activity is set to

$$a_{H2} = 0$$

Oxygen boundary conditions:

Similarly, on Membrane boundaries adjacent to oxygen Gas Phase domains, the oxygen activity a_{O2} is set as follows

$$a_{O2} = \frac{p_{O2(g)}}{p_{ref}}$$

where $p_{O2(g)}$ is the oxygen partial pressure in the adjacent gas phase. Oxygen is assumed to be instantly reduced when it reaches an electrode on the hydrogen gas side. On Membrane boundaries adjacent to hydrogen Gas Diffusion Electrode domains (or hydrogen Thin Gas Diffusion Electrode boundaries), the oxygen activity is set to

$$a_{O2} = 0$$

Nitrogen boundary conditions:

On Membrane boundaries adjacent to any Gas Phase domain, the nitrogen activity a_{N2} is set to

$$a_{N2} = \frac{p_{N2(g)}}{p_{ref}}$$

CONTRIBUTIONS TO CURRENT DISTRIBUTION MODEL

For the adjacent oxygen gas diffusion electrode boundaries where $a_{H2,mem}$ is set to 0, the corresponding oxidation charge transfer reaction will give rise to a local crossover current density i_{loc} according to

$$i_{loc} = \frac{nF(\mathbf{n} \cdot \mathbf{J}_{H2,\,mem})}{\nu_{H2}}$$

Similarly, the local crossover current density i_{loc} on adjacent hydrogen gas diffusion electrode boundaries becomes

$$i_{loc} = \frac{nF(\mathbf{n} \cdot \mathbf{J}_{O2,\,mem})}{\nu_{O2}}$$

The local crossover current density is added as normal current density contributions for the electronic and electrolyte potentials, respectively:

$$\mathbf{n} \cdot \mathbf{i}_l = i_{loc}$$

$$\mathbf{n} \cdot \mathbf{i}_s = -i_{loc}$$

Parasitic reactions not involving the H2/O2 species are not added by default, but may be added as ordinary electrode reactions in gas diffusion electrodes.

HEAT OF REACTIONS

The parasitic reactions of the H2/O2 species also give rise to boundary heat sources. The thermoneutral potential E_{therm} is defined as

$$E_{therm} = \frac{-\Delta_r H}{nF} - E_{eq,RHE}$$

where n is the number of electrons included in the electrode reaction, and the corresponding heat source Q_b is defined as

$$Q_b = i_{loc}(\phi_s - \phi_l - E_{therm})$$

CONTRIBUTIONS TO GAS DIFFUSION AND MOMENTUM TRANSFER MODEL

The species crossover flux will have an impact on the gas phase flux. For hydrogen, on the Membrane boundary adjacent to the hydrogen Gas Phase domain, the following flux contribution is added. Similarly, for oxygen, on the Membrane boundary adjacent to the oxygen Gas Phase domain, the following flux contribution is added For

nitrogen, on Membrane boundaries adjacent to any Gas Phase domain, the following flux contribution is added

$$\mathbf{n} \cdot (\mathbf{j}_i + \rho u_s \omega_i \mathbf{n}) = \mathbf{n} \cdot (M_i \mathbf{J}_{i,\,\text{mem}})$$

The above contributions are also added to the momentum transfer equation and Stefan velocity as

$$\mathbf{n} \cdot \rho \mathbf{u} = \sum_i \mathbf{n} \cdot (M_i \mathbf{J}_{i,\,\text{mem}})$$

$$\rho u_s = -\mathbf{n} \cdot \sum_i (\mathbf{j}_i + \rho u_s \omega_i \mathbf{n})$$

For any gas species participating in the parasitic hydrogen oxidation or oxygen reduction reaction, the corresponding mass flux contribution, on Membrane boundaries adjacent to H2/O2 Gas Diffusion Electrode domains or H2/O2 Thin Gas Diffusion Electrode boundaries, is

$$\mathbf{n} \cdot (\mathbf{j}_i + \rho u_s \omega_i \mathbf{n}) = -\frac{M_i \nu_i i_{\text{loc}}}{nF}$$

The above contribution is also added to the momentum transfer equation and Stefan velocity as

$$\mathbf{n} \cdot \rho \mathbf{u} = \sum_i -\frac{M_i \nu_i i_{\text{loc}}}{nF}$$

$$\rho u_s = -\mathbf{n} \cdot \sum_i (\mathbf{j}_i + \rho u_s \omega_i \mathbf{n})$$

Electroosmotic Water Drag Theory

In polymer electrolytes, ion transport and water transport are strongly intercoupled. As a result of this intercoupling, the water content of a polymer electrolyte impacts electrolyte conductivity. Accurate models of the electrolyte water content are hence paramount for polymer electrolyte-based fuel cell or electrolyzer modeling.

MEMBRANE WATER TRANSPORT MODEL

A complication when modeling the water-ion-polymer system is that the water-ion friction forces need to be taken into account in the transport equations both for the ions as well as the water molecules. The Weber-Newman model (Ref. 7) is based on concentrated solution theory, taking into account all three binary interactions between the charge-carrying ion, the immobilized polymer matrix and the water molecules. The model introduces the chemical potential of water in the polymer μ_0 (J/mol) as dependent variable, and defines the polymer water flux, $\mathbf{N}_0$ (mol/(m^2·s)), as

$$\mathbf{N}_0 = -\frac{\sigma_l \xi}{F} \nabla \phi_l + \left(\alpha + \frac{\sigma_l \xi^2}{F^2} \right) \nabla \mu_0$$

where ξ (dimensionless) is the electroosmotic coefficient and α (mol^2/(J·m·s)) the water transport coefficient, with the mass balance

$$\nabla \cdot \mathbf{N}_0 = 0$$

in the domain. The electrolyte phase charge balance equations gets a contribution from the water flux by adding a water flux term to the current vector as follows

$$\mathbf{i}_l = -\sigma_l \nabla \phi_l - \left(\frac{\sigma_l \xi}{F} \right) \nabla \mu_0$$

CHEMICAL POTENTIAL

The chemical potential driving force may generally be defined as

$$\nabla \mu_0 = RT \nabla \ln(a_0) + V_{H2O} \nabla p_{H2O(l)}$$

where a_0 is the thermodynamic activity of water, V_{H2O} is the partial molar volume of water, and $p_{H2O(l)}$ is the liquid water pressure. V_{H2O} is defined as

$$V_{H2O} = M_{H2O} / \rho_{H2O}$$

where M_{H2O} is the molar mass and ρ_{H2O} is the density of water at the operating temperature.

By integration, the chemical potential μ_0 is then defined as

$$\mu_0 = \mu_{0,\,ref} + RT \ln(a_0) + V_{H2O} p_{H2O(l)}$$

where $\mu_{0,ref}$ is a chosen reference potential, for convenience set to 0.

WATER ACTIVITY CORRELATIONS AND POLYMER ELECTROLYTE PROPERTIES

Many polymer electrolyte systems exhibit "Schröder's paradox," which refers to the phenomenon of strong hysteresis (path dependence) in water uptake when operating close to the dew point. Typically, an electrolyte membrane immersed in liquid water (liquid equilibrated) features significantly higher water uptake and conductivity compared to a previously dried membrane that has been hydrated in contact with water vapor at 100% relative humidity (vapor equilibrated).

For a vapor-equilibrated membrane, the parameters σ_l, ξ, and α typically all depend on the polymer water content. When measuring water uptake and other polymer electrolyte properties (such as σ_l, ξ, and α), it is common to report these versus the water activity, a_w, which is not the same as the thermodynamic activity a_0.

In the gas phase, a_w is defined as follows

$$a_w = \frac{p_{H2O(g)}}{p_{vap}(T)} = \frac{x_{H2O(g)} p_g}{p_{vap}(T)}$$

where is the $p_{H2O(g)}$ is the partial water pressure, p_{vap} is the vapor pressure, and p_g is the gas pressure. At an interface between a polymer electrolyte and the gas phase, assuming the polymer phase to be in equilibrium with the gas phase (and ideal gas conditions), the following condition holds

$$a_0 = x_{H2O(g)} \frac{p_g}{p_g^0} = \frac{p_{vap}(T)}{p_g^0} a_w$$

where p_g^0 is the standard condition gas pressure (typically 1 atm or 1 bar). The corresponding water activity inside the polymer electrolyte for a vapor-equilibrated polymer, for which the liquid pressure $p_{H2O(l)}$ is 0, may hence be defined as

$$a_w = \frac{p_g^0}{p_{vap}(T)} a_0 = \frac{p_g^0}{p_{vap}(T)} \exp\left(\frac{\mu_0}{RT}\right)$$

For a liquid-equilibrated system a_w is equal to 1.

Gas diffusion electrodes typically have a large electrolyte-gas phase interface area, in combination with fairly short diffusion lengths in the transport direction perpendicular to the pore walls. The water activity in the polymer of the gas diffusion electrode may be approximated to always be in equilibrium with the adjacent gas phase in the pores.

Hence the expression for a_w in the gas phase may be used also for the polymer in gas diffusion electrodes, and μ_0 need not to be solved for explicitly.

ABSORPTION-DESORPTION BOUNDARY CONDITIONS

As a result of the definition of the chemical potential, both the liquid pressure and the thermodynamic activity of water need to be considered when defining boundary conditions for water absorption-desorption at a Membrane boundary.

For a membrane in contact with vapor, the liquid pressure $p_{H2O(l)}$ is 0 Pa, and the chemical potential μ_0 relates to the thermodynamic activity a_0 as

$$\mu_0 = RT\ln(a_0)$$

so that

$$a_0 = \exp\left(\frac{\mu_0}{RT}\right)$$

Experimentally, the interface between a membrane and the vapor phase is often seen to exhibit a mass transfer resistance, where the absorption rate $r_{abs,dsp}$ follows a relationship based on the difference in the thermodynamic water activity between the two phases, as follows

$$r_{abs,dsp} = k_{abs,dsp}\left(\frac{p_{H2O(g)}}{p_g^0} - a_0\right)$$

where $k_{abs,dsp}$ (mol/(m^2 s)) is a rate constant and the activity of water in the gas phase has been assumed to equal the partial pressure $p_{H2O(g)}$ divided by the standard condition pressure p_g^0 (ideal gas conditions).

The rate may then be added as a flux boundary condition according to

$$-\mathbf{n} \cdot \mathbf{N}_0 = r_{abs,dsp}$$

For a membrane in contact with liquid water, a_w is equal to 1. Interfaces of this kind have been empirically found to exhibit way lower mass transfer resistances than for the vapor case. For this case, the boundary condition may be formulated based on the liquid pressure $p_{H2O(l)}$ as

$$\mu_0 = RT\ln\left(\frac{p_{vap}(T)}{p_g^0}\right) + V_{H2O}p_{H2O(l)}$$

For this cases the absorption rate $r_{abs,dsp}$ can be evaluated at the boundary as

$$r_{abs,dsp} = -\mathbf{n} \cdot \mathbf{N}_0$$

The absorbed-desorbed water adds to the boundary mass flux of the neighboring gas phase according to

$$\mathbf{n} \cdot (\mathbf{j}_{H2O} + \rho u_s \omega_{H2O} \mathbf{n}) = -M_{H2O} r_{abs,dsp}$$

The water may be transported into the gas phase domain in either the liquid water phase or as vapor. The above contribution is also added to the momentum transfer equation and Stefan velocity as

$$\mathbf{n} \cdot \rho \mathbf{u} = -M_{H2O} r_{abs,dsp}$$

$$\rho u_s = -\mathbf{n} \cdot (\mathbf{j}_{H2O} + \rho u_s \omega_{H2O} \mathbf{n})$$

HEAT OF WATER ABSORPTION

The boundary heat source Q_b due to the absorption-desorption is defined as

$$Q_b = r_{abs,dsp} \Delta_r H_{abs(g)}$$

where $\Delta_r H_{abs(g)}$ is the heat of absorption for vapor into the polymer electrolyte. If the water transport occurs in the liquid phase, the heat source becomes

$$Q_b = r_{abs,dsp} (\Delta_r H_{abs(g)} + \Delta_r H_{vap}(T))$$

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4

Electrochemistry Interfaces

This chapter describes the physics interfaces found under the **Electrochemistry** branch ( ).

In this chapter:

The Primary and Secondary Current Distribution Interfaces

In this section:

- The Primary Current Distribution and Secondary Current Distribution Interfaces
- Electrolyte
- Initial Values
- Porous Electrode
- Periodic Condition
- Thin Electrolyte Layer
- Edge Electrode

- Electrode Line Current Source
- Electrolyte Line Current Source
- Electrode Symmetry Axis Current Source
- Electrolyte Symmetry Axis Current Source
- Electrode Point Current Source
- Electrolyte Point Current Source

🔍   Only the physics interface-specific nodes are described here. All other nodes in the Primary Current Distribution and Secondary Current Distribution interfaces are described in Shared Physics Features in the Current Distribution Interfaces

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The Primary Current Distribution and Secondary Current Distribution Interfaces

The **Primary Current Distribution (cd)** interface (〚 〛) and the **Secondary Current Distribution (cd)** interface (〚 〛) are found under the **Electrochemistry** branch (〚 〛) when adding a physics interface.

Primary Current Distribution Interface

The **Primary Current Distribution** interface defines the transport of charged ions in an electrolyte of uniform composition as well as current conduction in electrodes using Ohm's law in combination with a charge balance. The physics interface neglects activation overpotentials due to charge transfer reactions.

Use this physics interface to estimate the ohmic losses in simplified models of electrochemical cells, where the overpotentials of the electrode reactions are small compared to the ohmic voltage drops in the electrolyte and electrodes.

Secondary Current Distribution Interface

The **Secondary Current Distribution** interface is similar to the Primary Current Distribution interface, except that it also accounts for activation overpotentials. The relation between charge transfer and overpotential can be described using arbitrary kinetic expressions, such as Butler–Volmer and Tafel equations.

Use this physics interface for generic modeling of electrochemical cells. It can be combined with interfaces modeling mass transport to describe concentration dependent (tertiary) current distributions.

Use the **Current Distribution Type** setting on the physics interface node, described below, to switch between a Primary Current Distribution and a Secondary Current Distribution interface.

	• Introduction to Electrochemistry Modeling

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 `cd`.

DOMAIN SELECTION

	Domains that do not conduct current should be omitted from the Domain Selection: for example, the gas channels in a fuel cell.

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.

CURRENT DISTRIBUTION TYPE

The **Current Distribution Type** selected in the list is based on the choice made when adding a physics interface — **Primary** or **Secondary**. The Primary Current Distribution interface changes to a Secondary Current Distribution interface if the choice is changed to **Secondary**, and vice versa.

The selection between **Primary** or **Secondary** governs how electrode reactions are modeled on interfaces between electrodes and electrolytes.

- Models using a **Primary** current distribution type use potential constraints (Dirichlet boundary conditions), according to the equilibrium potential setting.
- **Secondary** current distribution models use current flux conditions (Neumann boundary conditions) according to the sum of all electrode reaction current densities.

PHYSICS VS. MATERIALS REFERENCE ELECTRODE POTENTIAL

The **Physics vs. Materials Reference Electrode Potential** setting on the physics interface node can be used to combine material library data for current densities and equilibrium potentials with an arbitrary reference electrode scale in the physics. The setting affects the electrode potentials used for model input into the materials node, as well as all equilibrium potential values output from the materials node.

Note that the setting will only impact how potentials are interpreted in communication between the physics and the **Materials** node. If the **From material** option is not in use for equilibrium potentials or electrode kinetics, the setting has no impact.

DEPENDENT VARIABLES

This physics interface defines dependent variables (fields) for the **Electrolyte potential** and **Electric potential**. The names can be changed but the names of fields and dependent variables must be unique within a model.

DISCRETIZATION

The interface uses **Linear** elements by default and this setting is recommended for most problems. Certain types of problems, such as models using porous electrodes, or current distribution problems in two dimensions or higher, may benefit in terms of solution accuracy from using **Quadratic** elements.

In multiphysics models it is generally recommended to use the same element order in all coupled interfaces.

To see all settings in this section, click the **Show More Options** button (☞) and select **Advanced Physics Options** in the **Show More Options** dialog box.

⌕	• Electrochemical Reactions and the Difference Between a Primary and a Secondary Current Distribution • Domain Equations for Primary and Secondary Current Distributions • Shared Physics Features in the Current Distribution Interfaces • Theory for the Current Distribution Interfaces

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Electrolyte

Use the **Electrolyte** node to define an electrolyte domain that only conducts current in the ion conducting phase.

Note that electrolyte in this case does not refer to the pore electrolyte in porous electrodes (which should be defined by a Porous Electrode node instead).

The **Electrolyte conductivity**, σ_l (SI unit: S/m), parameter will define how the current in the domain depends on the gradient of the potential.

Initial Values

Use this node to specify the **Initial Values** of the electrolyte potential and the electric potential for the solver.

For many electrochemical problems that use nonlinear electrode kinetics, such as Butler–Volmer kinetics, providing reasonable initial values can significantly improve solver convergence.

A good value for the **Electric potential** (SI unit: V) in electrode and porous electrode domains can usually be derived from the boundary conditions. For instance, if a boundary has been grounded or set to a cell potential, use that value as the initial value also in the adjacent domain. For the **Electrolyte potential** (SI unit: V) a good initial value is often the negative of the equilibrium potential of the grounded electrode.

Note: For **Primary** current distributions, or for models solved using a **Current Distribution Initialization** study step set to **Primary**, the settings of this section usually have limited impact on the solver convergence.

Porous Electrode

The **Porous Electrode** node sets up charge balances for the electrode and the pore electrolyte in a porous electrode. Note that the node should be used for porous domains that conduct current in both an electrolyte and an electrode phase. For the case of domains that do not contain a pore electrolyte — for instance, a current collector/feeder or a gas diffusion layer (GDL) in a fuel cell — use an Electrode node instead.

Use Porous Electrode Reaction subnodes to define the charge transfer reactions that occur on the interface between the electrolyte and electrode phases within the porous electrode. For the Secondary Current Distribution interface, the Porous Matrix Double-Layer Capacitance subnode is also available.

The conductivities are taken **From material** by default. From the respective material list you may any material in the model, if present. By default they are set to the **Domain material** (which is the material applied to the active domain in the **Materials** node).

You may use the **Effective conductivity correction** factors to account for the lowered effective conductivities of the electrode and electrolyte phases due to the lower volume fractions of each phase, and the tortuosity of the porous matrix.

The **Electrode volume fraction** is used to calculate the effective electrical conductivity of the porous matrix when the correction factor is set to **Bruggeman** or **Tortuosity**. Additionally, it is used in calculating the active specific surface area of the porous matrix when **Particle-based area** option is selected in the child nodes.

DISSOLVING-DEPOSITING SPECIES

Use the settings of this section to define species that participate in dissolution-deposition electrode reactions within the porous electrode, for instance metal deposition/dissolution or oxide formation.

Use the **Add** (+) and **Delete** (≡x) buttons as needed in the tables to control the number of species.

Dependent variables for the volumetric molar concentration are added for each dissolving-depositing species. These variables can be used to keep track of the amount of reacted material in the porous electrode. The total molar dissolution/deposition rate depends on the reaction rates and stoichiometry, defined in the **Porous Electrode Reaction** subnodes.

The **Density** and **Molar mass** determine the electrode growth velocity and the resulting dissolved/deposited layer thickness. By multiplying by the electrode surface area (in the case of multiple electrode reaction the average surface area is used), the change in electrode and electrolyte volume fractions can be also be calculated. By use of the **Add volume change to electrode volume fraction** (not available for Separator node of Tertiary Current Distribution interface) and **Subtract volume change from electrolyte volume fraction** check boxes you may define how these volume changes should be included in the model.

Thickness variables, based on the surface area, are also defined that you for instance can use to couple to the Film Resistance (see below).

FILM RESISTANCE

See the Electrode Surface node.

	• Domain Equations for Primary and Secondary Current Distributions
🔍	• Porous Electrode Theory

Periodic Condition

Use the **Periodic Condition** to define a periodic relation between two boundaries — for instance, in a model describing a repetitive unit cell.

Use the **Apply for electrolyte phase** and **Apply for electrolyte** check boxes to enable the periodic condition for the electrolyte and electrode phase potentials, respectively.

By specifying a **Potential difference,** an offset in potential (typically per unit cell) can be prescribed.

For more information, see Periodic Boundary Conditions in the *COMSOL Multiphysics Reference Manual*.

Thin Electrolyte Layer

The Thin Electrolyte Layer node can be used to model a thin insulating or resistive sheet, located on an interior boundary in an electrolyte domain. The node can be used as an alternative to drawing the actual layer domain in the model geometry, which may significantly reduce meshing and solver time, especially in 3D models.

Thin insulating sheets are commonly inserted in the electrolyte in various types of electrochemical cells. For example they may be used for optimizing the current distribution in a corrosion protection application, of for optimizing the local deposition rate in a deposition bath.

The layer may be set to be either **Insulating** or **Resistive**.

For the case of **Resistive**, the **Surface Resistance** can either be set directly, or calculated from **Thickness and Conductivity** values.

ADVANCED SETTINGS

Enable **Slit electric potential in porous electrodes** to make the layer fully insulating for the electrode phase potential along the selected boundaries.

Edge Electrode

The **Edge Electrode** can be used in 3D problems to define electrodes such as long pipes and thin wires where the electric potential variation within the electrode in the normal direction to the electrode surface is negligible. This assumption allows for the thin electrode domain to be replaced by a lumped one-dimensional partial differential equation formulation on the edge, describing an electrode surface along the edge with a given **Edge electrode radius**. In this way the problem size can be reduced, and potential problems with mesh anisotropy in the thin layer can be avoided.

The electric current conduction in the tangential direction of an edge can be described by **Ohm's law** or a **Fixed** electric potential or a **Floating potential** assuming infinite conductivity of the edge or an **External short** electric potential which allows to connect two electrodes over an external connector with a given bulk resistance or a **Connection point** electric potential which allows to define a location for connections to other locations in the model.

An Edge Electrode can only be applied to edges within, or adjacent to, Electrolyte domains.

A default Electrode Reaction subnode is added by default to the feature. **Double Layer Capacitance**, **Electric Ground**, **Electric Potential**, and **Electrode Current** subnodes can also be added to the feature.

FILM RESISTANCE

See the Electrode Surface node. The section is only available when a **Secondary** current distribution has been selected on the parent node.

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 mesh size in the perpendicular direction to the edge should preferably be in the same order of magnitude as the **Edge electrode diameter** in order to achieve good numerical accuracy.

Electrode Line Current Source

For 3D components, use the **Electrode Line Current Source** on edges.

For 2D components use it on points.

For 2D axisymmetric components, it can only be selected on points outside the symmetry axis.

ELECTRODE CURRENT SOURCE
Enter the **Electrode current source** $q_{1,s}$ (SI unit: A/m). The default is 0 A/m.

Electrolyte Line Current Source

For 3D components, use the **Electrolyte Line Current Source** on edges.

For 2D components use it on points.

For 2D axisymmetric components, it can only be selected on points outside the symmetry axis.

ELECTROLYTE CURRENT SOURCE
Enter the **Electrolyte current source** $q_{1,l}$ (SI unit: A/m). The default is 0 A/m.

Electrode Symmetry Axis Current Source

For 2D axisymmetric components apply an **Electrode Symmetry Axis Current Source** along the symmetry axis boundary.

ELECTRODE CURRENT SOURCE
Enter the **Electrode current source** $q_{1,s}$ (SI unit: A/m). The default is 0 A/m.

Electrolyte Symmetry Axis Current Source

	For 2D axisymmetric components apply an **Electrolyte Symmetry Axis Current Source** along the symmetry axis boundary.

ELECTROLYTE CURRENT SOURCE

Enter the **Electrolyte current source** $q_{l,l}$ (SI unit: A/m). The default is 0 A/m.

Electrode Point Current Source

	For 3D components, use the **Electrode Points Current Source** on edges.
	For 2D axisymmetric components, it can only be selected on points located on the symmetry axis.

ELECTRODE CURRENT SOURCE

Enter the **Electrode current source** $q_{p,s}$ (SI unit: A). The default is 0 A.

Electrolyte Point Current Source

	For 3D components, use the **Electrolyte Points Current Source** on edges.
	For 2D axisymmetric components, it can only be selected on points located on the symmetry axis.

ELECTROLYTE CURRENT SOURCE

Enter the **Electrolyte current source** $q_{p,l}$ (SI unit: A). The default is 0 A.

Electrode Current

Use this node to define a current source in a point of an Edge Electrode node.

This node is available as a subnode to the **Edge Electrode** node, when **Ohm's Law** has been selected as the electric potential model.

The Tertiary Current Distribution, Nernst–Planck Interface

In this section:

- The Tertiary Current Distribution, Nernst–Planck Interface
- Electrolyte
- Porous Electrode
- Separator
- Reactions
- Thin Electrolyte Layer
- Initial Values

Various nodes are also available and described for the Transport of Diluted Species interface. See Domain, Boundary, and Pair Nodes for the Transport of Diluted Species Interface

	All other nodes in the Tertiary Current Distribution, Nernst–Planck interface are described in Shared Physics Features in the Current Distribution Interfaces

The Tertiary Current Distribution, Nernst–Planck Interface

The **Tertiary Current Distribution, Nernst-Planck (tcd)** interface ( ), found under the **Electrochemistry** branch ( ) when adding a physics interface, describes the current and potential distribution in an electrochemical cell taking into account the individual transport of charged species (ions) and uncharged species in the electrolyte due to diffusion, migration, and convection using the Nernst–Planck equations. The physics interface supports different descriptions of the coupled charge and mass transport in the electrolyte (see Electrolyte Charge Conservation below). The electrode kinetics for the charge transfer reactions can be described by using arbitrary expressions or by using the predefined Butler–Volmer and Tafel expressions.

Ohm's law is used in combination with a charge balance to describe the flow of currents in the electrodes. The charge transfer reactions can be defined as boundary

conditions or as sources or sinks within a domain in order for the case of porous electrodes.

$\circledcirc$ Introduction to Electrochemistry Modeling

SETTINGS

The **Label** is the physics interface node name that will be shown in the model builder tree.

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 `tcd`.

DOMAIN SELECTION

The domains that do not conduct current should be omitted from the selection list, for example, the gas channels in a fuel cell.

OUT-OF-PLANE THICKNESS

For 2D components, the **Thickness** field (default value: 1 m) defines a parameter for the thickness of the geometry perpendicular to the two-dimensional cross-section. 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.

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.

ELECTROLYTE CHARGE CONSERVATION

The physics interface features five different descriptions of the coupled charge and mass transport in the electrolyte.

Use the **Electroneutrality** or the **Electroneutrality, water based** charge conservation option to model cells with significant concentration gradients of the current-carrying species (ions). The electroneutrality condition implicitly assumes that all major current-carrying ions are included in the model. In addition to the electroneutrality condition, the **Electroneutrality, water based** option also adds the water auto-ionization equilibrium condition, including proton and hydroxide transport, when defining the electrolyte equations. Note that this option adds the concentration variables for protons (`tcd.cH`) and hydroxide (`tcd.OH`) automatically, and that dependent variables for these two species should not be added under **Dependent Variables** below. With this setting, to control the initial pH in a simulation, set the initial concentrations of the other ions in the simulation such that the matching concentration of protons and hydroxide ions matches the pH desired. For pH less than 7, add and set the concentration of anions. For pH more than 7, add and set the concentration of cations. For example, for a water-based system with only Cl-, an initial concentration for Cl- of 10^{-5} M will result in an initial pH of 5. This is analogous to acidifying the solution using HCl.

A **Supporting electrolyte** describes a situation where the major part of the charge is transferred by ions whose concentration can be described as constant.

Use the **Electroanalysis** (no potential gradients) option to model electroanalytical problems with electrolyte solutions containing a large quantity of inert supporting electrolyte, with a conductivity so high that ohmic losses can be assumed to be negligible. The electroanalysis option will not solve for the electrolyte potential as a dependent variable, setting it to a constant value of 0. Migration effects are hence neglected. Domain and boundary nodes only applicable to the electrolyte phase potential will be disabled when using electroanalysis.

The **Poisson** option couples the Nernst–Planck equations for mass transport to the Poisson equation for describing the potential distribution in the electrolyte, without any assumption of electroneutrality. This option is typically used when modeling problems where charge separation effects are of interest, typically within nanometers from an electrode surface.

For the Electroneutrality option, the **From electroneutrality** list sets the species that is calculated from the corresponding condition. Note that the choice of species to be taken from electroneutrality affects the specific boundary conditions that can be set on the eliminated species. For example, flux and concentration settings cannot be set for the eliminated species, and initial values cannot be provided. The choice can also have an impact on the numerics of the problem.

A general advice is to choose a relatively inert ion with high mole fraction to be taken from electroneutrality for best numerical results.

PHYSICS VS. MATERIALS REFERENCE ELECTRODE POTENTIAL

The **Physics vs. Materials Reference Electrode Potential** setting on the physics interface node can be used to combine material library data for current densities and equilibrium potentials with an arbitrary reference electrode scale in the physics. The setting affects the electrode potentials used for model input into the materials node, as well as all equilibrium potential values output from the materials node.

Note that the setting will only impact how potentials are interpreted in communication between the physics and the **Materials** node. If the **From material** option is not in use for equilibrium potentials or electrode kinetics, the setting has no impact.

DEPENDENT VARIABLES

This physics interface defines these dependent variables (fields), the **Concentrations** of the species, the **Electrolyte potential**, and the **Electric potential**.

The names can be changed but the names of fields and dependent variables must be unique within a model.

DISCRETIZATION

Concentrations basis function orders higher than **Quadratic** are not recommended if transport by convection is dominating in the model.

To see all settings in this section, click the **Show More Options** button (👁) and select **Advanced Physics Options** from the **Show More Options** dialog box.

CONSISTENT STABILIZATION AND INCONSISTENT STABILIZATION

To display these sections, click the **Show More Options** button (👁) and select **Stabilization** from the **Show More Options** dialog box. There are two consistent stabilization methods available and selected by default — **Streamline diffusion** and **Crosswind diffusion**. There is one inconsistent stabilization method, **Isotropic diffusion**,

which is not selected by default. Any settings unique to this physics interface are listed below.

- When the **Crosswind diffusion** check box is selected, a weak term that reduces spurious oscillations is added to the transport equation. The resulting system is nonlinear. There are two options for **Crosswind diffusion type**:

  - **Do Carmo and Galeão** — the default option. This type of crosswind diffusion reduces undershoot and overshoot to a minimum but can in rare cases give equations 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 undershoot and overshoot. It is also less effective for anisotropic meshes. The Codina option activates a text field for the **Lower gradient limit** g_{lim} (SI unit: mol/m^4). 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 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.

> [!]
> 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.

> 🔍
> - The Nernst–Planck Equations
> - Domain Equations for Tertiary Current Distributions Using the Nernst–Planck Equations and Electroneutrality
> - Shared Physics Features in the Current Distribution Interfaces
> - Theory for the Current Distribution Interfaces

Electrolyte

Use the **Electrolyte** node to define an electrolyte domain that only conducts current in the ion conducting phase. The combined charge and mass transfer in the electrolyte is defined by the node.

What settings are available in this node depends on the Electrolyte Charge Conservation setting, available on the top node. The **Electrolyte conductivity** (SI unit: S/n) setting is only available for the **Supporting Electrolyte** option. Diffusivity and mobility settings for H^+ and OH^- are only available for the **Electroneutrality, water-based** option.

The **Convection** section is available when the **Convection** check box is selected on the interface top node. The **Velocity field u** (SI unit: m/s) of the solvent is specified as a feature input. Select the source of velocity field from the velocity field list.

By default the **Mobility** (SI unit: s·mol/kg) for each species is set to be calculated based on the diffusion coefficients (SI unit: m^2/s) specified in the **Diffusion** section and the temperature using the **Nernst-Einstein relation**.

The mobility setting will only have an impact on the transport by migration of charged species, as defined by the **Charge number** z_c (dimensionless, specify negative charges using a minus sign). For the **Electroneutrality** charge conservation model you need at least one positively and one negatively charged species (ion) in the electrolyte.

Specify the temperature (if you are using mobilities based on the **Nernst-Einstein relation**) in the **Model Inputs** section.

The **Water Self-ionization** section is available for the **Electroneutrality, water-based** option. The section allows the water self-ionization constant to be set. Using the **Built in** option, the constant will be set to account for temperature, giving the pH of the simulation the correct temperature dependence.

Note that the electrolyte in this case does not refer to the pore electrolyte in porous electrodes (which should be defined by a Porous Electrode node instead). For porous separators, use the Separator instead.

	• Electrolyte Theory
🔍	• Domain Equations for Tertiary Current Distributions Using the Nernst–Planck Equations and Electroneutrality

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Porous Electrode

The **Porous Electrode** node sets up charge balances for the electrode and the pore electrolyte in a porous electrode, and as well as the mass balance for the species in the electrolyte.

Note that the node should be used for porous domains that conduct current in both an electrolyte and an electrode phase. For the case of domains that do not contain a pore electrolyte — for instance, the gas diffusion layer (GDL) in a PEMFC electrode — use an Electrode node instead.

Use Porous Electrode Reaction child nodes to define the charge transfer reactions that occur on the interface between the electrolyte and electrode phases within the porous electrode. The Porous Matrix Double Layer Capacitance subnode is also available.

See the Electrolyte node for more information about the **Diffusion** and **Migration in Electric Field** settings of this node.

Correction factors may be specified in the **Effective Transport Parameter Correction** section to account for the lowered effective conductivities of the electrode and electrolyte phases due to the lower volume fractions of each phase, and the tortuosity of the porous matrix.

The **Electrode volume fraction** is used to calculate the effective electrical conductivity of the porous matrix when the correction factor is set to **Bruggeman** or **Tortuosity**. Additionally, it is used in calculating the active specific surface area of the porous matrix when **Particle-based area** option is selected in the child nodes.

DISSOLVING-DEPOSITING SPECIES
See the **Porous Electrode** node of The Primary and Secondary Current Distribution Interfaces

FILM RESISTANCE
See the Electrode Surface node.

⊙	• Porous Electrode Theory • Porous Electrode Reactions Theory • Domain Equations for Tertiary Current Distributions Using the Nernst–Planck Equations and Electroneutrality

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Separator

Use a **Separator** node to model electrolyte charge and mass transport in an electronically isolating porous matrix. Use correction factors to account for the lowered diffusion coefficients in the electrolyte and the lowered conductivities of the

electrode, due to the lower volume fractions of each phase and the tortuosity of the porous matrix.

See also the Electrolyte node for more information about the **Diffusion** and **Migration in Electric Field** settings of this node.

DISSOLVING-DEPOSITING SPECIES

See the **Porous Electrode** node of The Primary and Secondary Current Distribution Interfaces

Reactions

Use the **Reactions** node to define nonelectrochemical reactions in an electrolyte domain.

The node is found from the **Additional Sources** submenu.

REACTING VOLUME

When specifying reaction rates in the R_{c2} (SI unit: mol/m^3·s) fields for a species in a Porous Electrode domain, the specified reaction rate expression may either refer to the total volume or the pore (electrolyte) volume. For nonporous domains the settings of the Reacting Volume section has no impact.

For **Total volume** the reaction expressions are used as specified (multiplied by unity).

For **Pore volume** this results in the specified reaction expressions being multiplied by the domain electrolyte volume fraction ε_l. (ε_l equals unity for nonporous domains).

Initial Values

Use this node to specify the **Initial Values** of the concentration, electrolyte potential and electric potential dependent variables to be used by the solver.

For many electrochemical problems that use nonlinear electrode kinetics, such as Butler–Volmer kinetics, providing reasonable initial values can significantly improve solver convergence.

A good value for the **Electric potential** (SI unit: V) in electrode and porous electrode domains can usually be derived from the boundary conditions. For instance, if a boundary has been grounded or set to a cell potential, use that value as the initial value also in the adjacent domain. For the **Electrolyte potential** (SI unit: V) a good initial value is often the negative of the equilibrium potential of the grounded electrode.

For the **Concentration** initial values, at least one positive and one negative charged species should have a nonzero and positive initial value (after considering the electroneutrality condition). The initial value for the ion calculated from the electroneutrality condition cannot be set explicitly.

Ion Exchange Membrane

Use the ion exchange membrane node to specify a domain with a permanent fixed space charge. The node is typically used for defining permselective membranes, used for various applications such as dialysis cells or flow batteries.

The node models the transport of all species added at the interface top node, and adds a fixed space charge to the electroneutrality condition.

The **Fixed space charge** specifies the charge ions fixed in the membrane polymer matrix. Use negative space charges for cation selective membranes and positive charges for anion selective membranes, respectively.

Select the **Apply Donnan Boundary Conditions** check box to enable Donnan equilibrium conditions on all interior boundaries between the domain selected by the node and all adjacent domains selected by the interface (except **Electrode** nodes). The boundary conditions are applied for all species and the electrolyte potential dependent variable. This option is not available for the **Poisson** charge conservation model option.

For the remaining settings of this node, see the Electrolyte and Separator nodes.

Ion Exchange Membrane Boundary

Use the Ion Exchange Membrane boundary node to specify an external boundary over which the flux of a charge-carrying species is continuous but the electrolyte potential shifts with a specified value. This condition is typically used in electrochemical cells containing both free electrolytes and ion exchange membranes, for instance in dialysis or flow battery problems. The node is typically used to couple two separate current distribution interfaces, where one of the interfaces models free electrolyte domain, and the other interface models the ion-exchange membrane domain.

Note that using the Ion Exchange Membrane domain node often is a more convenient modeling approach if the transported species in the free electrolyte and ion exchange membrane are the same.

The node is applicable to external boundaries to electrolyte domains. For defining ion-exchange membranes on an interior boundary between two electrolyte domains, use the Thin Electrolyte Layer node.

The choice of **Charge-carrying species concentration species** specifies that the current flowing over the boundary will be carried by this species (which must have a nonzero charge number). Use the **Membrane potential** setting to set the electrolyte potential on the membrane side of the boundary. Note that if this potential is set to the electrolyte potential of a Primary or Secondary Current Distribution interface, no additional settings are needed in that interface to set up the correct boundary condition.

The potential condition may be either **Donnan**, which will calculate the potential shift over the boundary based on the membrane charge carrying species concentration, or can be **User defined**.

Thin Electrolyte Layer

Use this node to specify a thin layer on an interior boundary between two electrolyte domains. The node can be used as an alternative to drawing the actual layer as a domain in the model geometry, which may significantly reduce meshing and solver time, especially in 3D models.

The layer may either be **Insulating**, **Resistive** (supporting electrolytes only), or an **Ion exchange membrane**.

For **Resistive** or **Ion exchange membrane**, the potential drop over the membrane is determined either from the **Surface resistivity** or the **Thickness and conductivity**.

For **Ion exchange membrane**, the choice of **Charge-carrying species concentration species** specifies that the current flowing over the layer will be carried by this species (which must have a nonzero charge number). The potential condition may be either **Donnan**, which calculates the potential shift over the boundary based on the membrane charge carrying species concentration, or **User defined**.

Shared Physics Features in the Current Distribution Interfaces

Domain, Boundary, Pair, Edge, and Point Nodes for the Electrochemistry Interfaces

This chapter describes various domain, boundary, edge, point, and pair nodes that are common to several of the Electrochemistry Interfaces interfaces.

The nodes are available from the **Physics** ribbon toolbar (Windows users), **Physics** context menu (macOS or Linux users), or right-click to access the context menu (all users).The nodes and features described in this section are available for all the Electrochemistry branch interfaces unless otherwise indicated.

	In general, to add a node, go to the **Physics** toolbar, no matter what operating system you are using. Subnodes are available by (right) clicking the parent node and selecting it from the **Attributes** menu.

- Circuit Terminal
- Double-Layer Capacitance
- Electric Ground
- Electric Potential
- Electric Reference Potential
- Current Conductor
- Electrode Current
- Electrode Current Density
- Electrode Current Source
- Electrode-Electrolyte Boundary Interface
- Electrode Potential
- Electrode Reaction
- Electrode Surface
- Electrolyte Current Density
- Electrolyte Current Source
- Electrolyte Potential
- External Short
- Harmonic Perturbation

- Highly Conductive Porous Electrode
- Initial Values for Adsorbing-Desorbing Species
- Initial Values for Dissolving-Depositing Species
- Insulation
- Perforated Electrode Surface
- Internal Electrode Surface
- Line Mass Source[1]
- Nonfaradaic Reactions
- Point Mass Source[1]
- Porous Electrode Reaction
- Porous Matrix Double-Layer Capacitance
- Reference Electrode
- Symmetry
- Thin Electrode Layer

[1] For the Tertiary Current Distribution, Nernst–Planck interface, these nodes are available and described 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. |

| 🔍 | Theory for the Current Distribution Interfaces |

Current Conductor

Use the **Current Conductor** node to define an electrode domain that only conducts current in the electron conducting phase.

The node is typically used for modeling solid metal electrodes, current collectors, current feeders, gas diffusion layers and gas backings.

The **Electrical conductivity** σ_s (SI unit: S/m) parameter will define how the current in the domain depends on the gradient of the potential.

Q	Electrode Theory

Highly Conductive Porous Electrode

The **Highly Conductive Porous Electrode** node defines a charge balance of the pore electrolyte in a porous electrode, and, for interfaces solving for electrolyte species, the corresponding mass balance for the species in the electrolyte. Use this node when electrical conductivity is high enough to assume uniform potential in the electron conducting phase of the porous electrode.

See the Electrode Surface node for a description of the Electrode Phase Potential Condition and Harmonic Perturbation sections.

See the node for a description of the remaining settings.

Electrode Current Source

Use the **Electrode Current Source** node to define contributions to the current density from electron current sources. The **Current source**, Q_s (SI unit: A/m^3), is added according to the following equation:

$$\nabla \cdot \mathbf{i}_s = Q_s$$

where

$$\mathbf{i}_s = -\sigma_s \nabla \phi_s$$

and σ_s denotes the electrode's conductivity and ϕ_s the electric potential.

To use this feature, click the **Show More Options** button (☞) and select **Advanced Physics Options** in the **Show More Options** dialog box. Then add the node from the **Additional Sources** submenu.

Electrolyte Current Source

Use the **Electrolyte Current Source** node to define contributions to the current density in the electrolyte from, for example reactions, or other effects.

The **Current source**, Q_l (SI unit: A/m^3), is added according to the following equation:

$$\nabla \cdot \mathbf{i}_l = Q_l$$

To use this feature, click the **Show More Options** button (☞) and select **Advanced Physics Options** in the **Show More Options** dialog box. Then add the node from the **Additional Sources** submenu.

Porous Electrode Reaction

The **Porous Electrode Reaction** node defines the electrode kinetics for a charge transfer reaction that occurs at the interface between the pore electrolyte and the electrode matrix a porous electrode. The node can be added as subnode to a **Porous Electrode** node. Add multiple nodes to the same **Porous Electrode** node to model multiple reactions, for instance in mixed potential problems.

See the Electrode Reaction node for a description of the Equilibrium Potential, Electrode Kinetics, Stoichiometric Coefficients and Heat of Reaction sections.

ACTIVE SPECIFIC SURFACE AREA

The **Active specific surface area**, a_v (SI unit: m^2/m^3) specifies the area of the electrode-electrolyte interface that is catalytically active for this porous electrode reaction. a_v is multiplied by i_{loc}, defined in the Electrode Kinetics section, to produce a current source in the domain.

This section is not available for primary current distribution interfaces.

⊙	• Porous Electrode Reactions Theory
	• Electrode Kinetics Expressions.

Porous Matrix Double-Layer Capacitance

Use the **Porous Matrix Double-Layer Capacitance** subnode to define a nonfaradaic double-layer current density at the interface between the porous electrode matrix and the electrolyte. The node can be added as subnode to a **Porous Electrode** node.

The resulting double-layer current source in the **Porous Electrode** domain depends on the time derivative of the potentials and is proportional to both the **Electrical double-layer capacitance** C_{dl} (SI unit: F/m^2) and the **Double-layer area** $a_{v,dl}$ (SI unit: 1/m).

Note that for stationary problems the double-layer current is zero.

This node is not available for the Primary Current Distribution interface.

Use the settings of the **Stoichiometry** section (not available in the Primary or Secondary Current Distribution interfaces) to control what species are participating in the double-layer charging — that is, the mass exchange between the double layer and the electrolyte outside the double layer.

Insulation

The **Insulation** boundary condition describes the walls of a cell or the boundaries of the cell that do not face a conductor. The boundary condition imposes the following equation:

$$\mathbf{i}_k \cdot \mathbf{n} = 0$$

where $\mathbf{i}_k$ denotes the current density vector and $k = l, s$ is an index for the electrolyte and electrode, respectively.

Symmetry

For the Primary Current Distribution and Secondary Current Distribution interfaces, the **Symmetry** boundary condition is identical to the Insulation condition.

For the Tertiary Current Distribution, Nernst–Planck interface, the **Symmetry** boundary condition imposes a no flux condition for the molar flux of species at a boundary.

🔍	Symmetry Theory

Electrode Surface

Use the **Electrode Surface** node to model an electrochemical electrode-electrolyte interface between an electrolyte domain and an electrode boundary where the electrode is not included explicitly as a domain in the model geometry. Set the electric potential of the electrode or specify a current condition that the potential of the electrode shall fulfill, and use subnodes to specify the Electrode Reaction and the Double-Layer Capacitance at the interface.

This node can only be applied on outer boundaries to electrolyte domains. For interior boundaries between electrolyte and electrode domains, use the Internal Electrode Surface node. For interior boundaries to electrolyte domains, use the Perforated Electrode Surface node.

DISSOLVING-DEPOSITING SPECIES

Use the settings of this section to define species that participate in dissolution-deposition electrode reactions, for instance metal deposition/dissolution or oxide formation.

Use the **Add** (+) and **Delete** (≡ₓ) buttons as needed in the table to control the number of species.

The **Density** and **Molar mass**, in conjunction with the reaction rates and stoichiometry, defined in the **Electrode Reaction** subnodes, determine the normal electrode growth rate.

When the **Solve for species concentrations variables** check box is checked, dependent variables for the molar surface concentration of the dissolving-depositing species are added. These can be used to model the thickness of a dissolving/depositing layer in a time-dependent simulation where the resulting deformation in the model geometry is small and will have negligible impact on the current distribution. In stationary studies, the molar surface concentration variables will be defined but not solved for by default.

When solving for the species concentration variables, corresponding thickness variables are defined that you for instance can use to couple to the Film Resistance (see below).

🔍	Deposition-Dissolution Rates, Growth Velocities, and Thicknesses on an Electrode Surface

ADSORBING-DESORBING SPECIES

Use the settings of this section to define species that may adsorb or desorb on the electrode surface during charge transfer, or nonfaradaic, reactions.

The **Density of sites parameter** will be used to set up the local surface mass balance equations for the fractional surface coverages.

Use the **Add** (+) and **Delete** (≡ₓ) buttons as needed in the table to control the number of species. The name of each adsorbing-desorbing **Species** may be edited in the first column of the table. Use a **Site occupancy number** larger than unity for species that occupy more than one site at the electrode surface.

According to the settings of the table, the fractional surface coverage variable names will be defined according to `xxx.theta_yyy_zzz` where `xxx` is the interface name, `yyy` the tag of the electrode surface node, and `zzz` the species name. The variable `xxx.thetafree_yyy` represents the fraction of free surface sites. These variable names may be used when defining kinetics parameters in Electrode Reaction subnodes.

💡	Use The Surface Reactions Interface to model surface diffusion.

FILM RESISTANCE

Use a film resistance if you want to include an additional potential drop due to an ohmic resistance at the interface between the electrode and the electrolyte, for instance due to build-up of insulating deposits.

Specify either a **Surface resistance** R_{film} (SI unit: $\Omega \cdot \mathrm{m}^2$) directly or choose the **Thickness and conductivity** option to calculate the surface resistivity based on a depositing film thickness.

HARMONIC PERTURBATION

Use this section in conjunction with AC Impedance study types to control the perturbation amplitude in the frequency domain.

The perturbation parameter is either **Electric potential**, **Electrode potential**, **Total current**, or **Average current density**, based on the **Boundary condition** selected in the next section.

The frequency spectrum is specified in the study node.

ELECTRODE PHASE POTENTIAL CONDITION

This section specifies the potential in the electrode phase of the electrolyte-electrode interface. The electrode potential is used (via the overpotential) by the **Electrode Reaction** subnodes.

Use the **Electric potential** option to set the value of the potential explicitly with respect to ground whereas the **Electrode potential** will set the potential value with respect to a reference potential. **Total current**, **Average current density**, and **External short** all add an extra global degree of freedom for the potential in the electrode phase, set to comply with the chosen condition.

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.

See also the documentation for the Electrode Potential and External Short nodes for further information about these boundary condition.

Cyclic Voltammetry

The **Cyclic voltammetry** setting varies the electric potential linearly in time as follows when used in conjunction with a Cyclic Voltammetry study step:
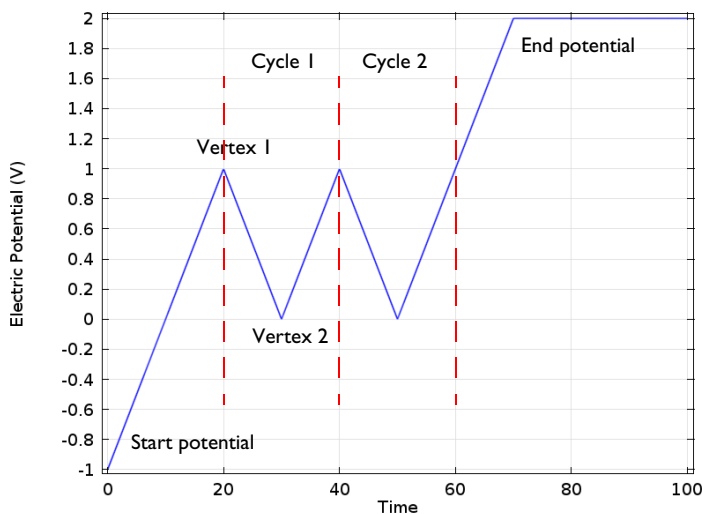
Figure 4-1: Electric potential vs time generated by the cyclic voltammogram boundary condition. The linear sweep rate is 100 mV/s, the number of cycles is 2. Potentials levels are also shown.

More advanced waveforms can be obtained using the **Electric potential** option with a parameter setting based on **Functions** found in the **Definitions** menu.

Counter Electrode (Electroanalysis Only)

This boundary condition is only available for the **Electroanalysis** charge conservation model in the **Tertiary Current Distribution, Nernst-Planck (tcd)** interface.

The **Counter electrode** option will set a potential to ensure an overall charge balance of the cell so that the integral of all electrode reaction currents of all electrode surface node sums up to zero.

See also Counter Electrodes and Overall Charge Balance

ADVANCED CYCLIC VOLTAMMETRY SETTINGS

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

If **Cyclic voltammetry** is selected as the **Boundary condition**, the check boxes **Add events at vertex potentials in cyclic voltammetry** and **Smoothing of cyclic voltammetry wave functions** are both selected by default.

When **Smoothing of cyclic voltammetry wave functions** is enabled, smoothing is applied on the triangular wave around the vertex potentials. The **Smoothing factor** defaults to $1 \cdot 10^{-3}$. The smoothing zone corresponds to the product of the smoothing factor with half the duration of one period of the triangular wave.

When **Add events at vertex potentials in cyclic voltammetry** is enabled, solver events are added at the vertex potentials for the cyclic voltammogram. When the vertex potentials are reached, these events cause the solver to stop, reinitialize some variables, and then continue. This typically improves solver convergence. In addition, by forcing the time-dependent solver to resolve the time steps when the vertex potentials are reached, the solution accuracy is improved, especially if the solver is set to output solutions before and after events.

EQUILIBRIUM POTENTIAL HANDLING (PRIMARY CONDITION)

This setting only has an effect if there are multiple Electrode Reaction subnodes present and if either a Current Distribution Initialization study step (using a Primary Current distribution type) or the Primary Current Distribution interface is used.

The setting determines which equilibrium potential value will be used for defining the primary current distribution constraint. When the **First reaction** has been selected, the first electrode reaction subnode must be active in the model.

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

CONSTRAINT SETTINGS

For primary current distributions, the use of weak constraints will in some cases give a more accurate value of the local current density during the solver process. This may in turn render more accurate results when coupling to the local current density variable to describe other phenomena in the model, for instance when modeling geometry deformation due to electrode dissolution/deposition.

The section is available in the Primary Current Distribution and Secondary Current Distribution interfaces when the **Current Distribution Model** property has been set to **Primary**.

This section is only available in the Primary Current Distribution and Secondary Current Distribution interfaces when the **Current Distribution Model** property has been

set to **Primary**. To display this section, click the **Show More Options** button (☛) and select **Advanced Physics Options** in the **Show More Options** dialog box.

🔍	• Electrode Reactions Theory • Film Resistance

Electrode Reaction

The **Electrode Reaction** subnode defines the electrode kinetics for a charge transfer reaction that occurs on an electrolyte-electrode interface boundary. Use multiple nodes to model multiple reactions, for instance in mixed potential problems.

The parent node may be either an Internal Electrode Surface or an Electrode Surface.

Note that all settings described below are not available for all Electrochemistry interfaces.

🔍	• Electrode Reactions Theory

EQUILIBRIUM POTENTIAL

The **Equilibrium potential**, E_{eq} (SI unit: V), is used in the electrode kinetics expressions in the Electrode Kinetics section (via the definition of the overpotential), or for setting up primary current distribution potential constraints.

The equilibrium potential may be defined either in the Materials node (**From material**), by using the **Nernst Equation**, or by using a **User defined** expression.

If the Nernst Equation is used, the concentration dependence is calculated automatically based on the **Reference equilibrium potential** $E_{eq, ref}$ (V).

For all interfaces except the Tertiary Current Distribution interface, the concentration dependence is based on the user-defined **Reduced species expression** C_R (unitless) and **Oxidized species expression** C_O (unitless) parameters. C_R and C_O should be defined so that the quotient between them is 1 for the reference state (for which $E_{eq}=E_{eq, ref}$).

In the Tertiary Current Distribution interface, the concentration dependence of the Nernst Equation is based entirely on the settings in the **Stoichiometric Coefficients** and the **Reference Concentrations** sections.

When using Nernst Equation, additional options are available in the **Butler-Volmer** expression type in the Electrode Kinetics section.

• Equilibrium Potentials and the Nernst Equation

REFERENCE CONCENTRATIONS

This section is only available in the Tertiary Current Distribution interface, if the equilibrium potential has been selected to be defined by the **Nernst Equation**.

The reference concentrations define the reference state for which $E_{eq} = E_{eq, ref}$.

ELECTRODE KINETICS

The settings of this section will define the local current density, i_{loc} (SI unit: A/m^2), at the interface between the electrolyte and the electrode. Note that i_{loc} for all built-in kinetics expression types will depend on the overpotential, which in turn depend on the Equilibrium potential defined in the previous section.

The **Local current density expression**, $i_{loc, expr}$ (SI unit: A/m^2), may be defined either in the Materials node (**From material**), by using the **From kinetics expression**, or by using a **User defined** expression.

For all kinetic expressions the **Exchange current density** i_0 (SI unit: A/m^2) is a measure of the kinetic activity. The exchange current density is typically concentration dependent.

Most kinetic expression types feature the **Limiting Current Density** option in order to impose an upper limit on the local current density magnitude. The feature can be used to model additional mass transport limitations that are not already included in the local current density expression. For **Limiting Current Density** enter a value for i_{lim} (SI unit: A/m^2).

In the Tertiary Current Distribution interface, the **Linearize concentration dependence for low concentrations** option is used to set a **Concentration linearization limit** c_{lim} (SI unit: mol/m^3) for linearizing the concentration dependence of kinetics for low concentrations, in order to improve convergence for nonunit stoichiometries. Note that this option is available for **Nernst Equation** equilibrium potential and **Butler-Volmer** kinetics with either **Mass action law** or **Lumped multistep** selected as the exchange current density type.

Butler–Volmer or Linearized Butler–Volmer

The Butler–Volmer kinetics expression is the most common way to define electrochemical kinetics. The **Linearized Butler–Volmer** is valid when the overpotentials of the reactions are small (<<25 mV). The linearized version can also be used to troubleshoot a model with convergence problems.

When using the **Nernst Equation** for defining the equilibrium potential (see above), the concentration dependence of the **Exchange current density** i_0 may be defined in a thermodynamically consistent way in accordance with the Nernst equation, in combination with a **Reference exchange current density** $i_{0,\mathrm{ref}}$ (A/m^2), which is the exchange current density when $E_{\mathrm{eq}}=E_{\mathrm{eq,\ ref}}$.

For all interfaces except the Tertiary Current Distribution interface, the concentration dependence when using **From Nernst Equation** will use C_R and C_O as preexponential factors for the anodic and cathodic terms, respectively. In the Tertiary Current Distribution interface, the **Lumped multistep** option can be used to define i_0 by the use of either **Generic** exponentials, or **Anodic** or **Cathodic** reaction orders. The **Mass action law** will define the reaction orders according to the reaction stoichiometry and the law of mass action.

The **Anodic transfer coefficient**, α_a (dimensionless), and **Cathodic transfer coefficient**, α_c (dimensionless), parameters will impact how much i_{loc} will change upon changes in the overpotential. In order to ensure thermodynamic consistency, α_c cannot be user defined when i_0 is calculated **From Nernst Equation** (or by **Mass action law** in the Tertiary Current Distribution interface). For this case, α_c is defined automatically, based on the number of participating electrons in the reaction, defined in the stoichiometry section.

Anodic Tafel Equation

This kinetics expression type neglects the cathodic (negative) term in the Butler–Volmer equation. It is only valid for electrode reactions with high anodic overpotentials (>>100 mV).

The **Anodic Tafel slope**, A_a (SI unit: V), defines the required increase in overpotential to result in a tenfold increase in the current density.

Cathodic Tafel Equation

This kinetics expression type neglects the anodic (positive) term in the Butler–Volmer equation. It is only valid for electrode reactions with significant cathodic overpotentials (<<-100 mV).

The **Cathodic Tafel slope**, A_c (SI unit: V), describes the required decrease in overpotential to result in a tenfold increase in the current density magnitude. A_c should be a negative value.

Concentration Dependent Kinetics
This expression type is not available if **Nernst equation** has been selected in the Equilibrium Potential section.

Note that the combination of **Nernst equation** and the **Butler-Volmer** kinetics type will in most cases render identical kinetics as for the Concentration Dependent Kinetics. It is recommended to always use Nernst Equation + Butler–Volmer whenever possible, since this combination is guaranteed to be thermodynamically consistent.

The Concentration Dependent Kinetics expression type may be used in concentration dependent (tertiary) current distribution problems. One or both of the **Oxidizing species expression** C_O (dimensionless) and **Reducing species expression** C_R (dimensionless) parameters may be concentration dependent, and should typically be defined so that $C_O = C_R$ at equilibrium.

⍰	• Electrode Kinetics Expressions

Fast Irreversible Electrode Reaction
This kinetics expression type is typically used in tertiary current distribution problems for reactions occurring far away from the equilibrium potential.

The kinetics expression type defines an irreversible electrode 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.

Thermodynamic Equilibrium (Primary Condition)
This choice imposes a zero overpotential for the electrode reaction by applying a constraint on the potential variables in order to comply with the equilibrium potential. Use this kinetics for very fast reactions.

In the Secondary Current Distribution interface the condition set by this expression type is mathematically identical to what is applied when a Primary Current

Distribution is chosen on the interface top node. The expression type can hence be used to mix primary and secondary current distributions on different electrodes. The Thermodynamic equilibrium (primary condition) cannot not be used when defining the kinetics for multiple electrode reactions at the same electrode in the Secondary Current Distribution interface.

STOICHIOMETRIC COEFFICIENTS

Specify the **Number of participating electrons** n_m in the electrode reaction and the **Stoichiometric coefficient** (v_{c1}, v_{c2}, and so forth) for each of the involved species according to the following generic electrochemical reaction:

$$\sum_{ox} v_{ox} S_{ox} + n e^- \Leftrightarrow \sum_{red} v_{red} S_{red} \tag{4-1}$$
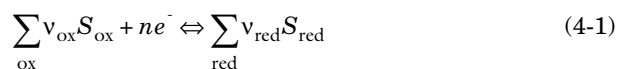
Set v_i as positive (v_{red}) for the reduced species and negative (v_{ox}) for the oxidized species in an electrochemical reaction. The number of participating electrons, n, should be positive.

If the concentration of a species in the charge conservation model for the electrolyte is based on an algebraic expression (such as the electroneutrality condition, or the water auto ionization), the stoichiometric coefficient for this species cannot be set explicitly. The stoichiometric coefficient will instead be set implicitly, based on the number of electrons and the stoichiometric coefficients of the other species participating in the reaction.

💡	An easy way to determine the stoichiometric coefficients for a reaction is to write the reaction as a reduction reaction (with the electrons on the left), irrespectively on the expected actual direction of the reaction in the model. The species on the left side then have negative coefficients and the species on the right have positive coefficients.
🔍	• Mass Fluxes and Sources Due to Electrochemical Reactions

HEAT OF REACTION

The **Heat of Reaction** section provides two options: **Temperature derivative** and **Thermoneutral voltage** to calculate the reversible heat source of the electrode reaction, which in turn can be used for coupling to heat transfer physics.

The **Temperature derivative of equilibrium potential** parameter, dE_{eq}/dT (SI unit: V/K), can be specified in case of **Temperature derivative** selection. Note that dE_{eq}/dT parameter value has no impact on the equilibrium potential variable.

The **Thermoneutral voltage** parameter, E_{therm} (SI unit: V), can be specified in case of **Thermoneutral voltage** selection.

🔍   •   Heating Due to Electrochemical Reactions

Double-Layer Capacitance

The **Double-Layer Capacitance** subnode describes the nonfaradaic currents due to charge and discharge of the double layer situated at the interface between the electrode and the electrolyte. The resulting double-layer current density on the boundary depends on the time derivative of the potentials and is proportional to the **Electrical double-layer capacitance** C_{dl} (SI unit: F/m^2). For stationary problems, the double-layer current density is zero.

Use this node to simulate transient analysis techniques, such as AC-impedance analysis and current interrupt studies.

The parent node may be either an Internal Electrode Surface or an Electrode Surface.

This subnode is not available for the Primary Current Distribution interface.

Use the settings of the **Stoichiometry** section (not available in the Primary or Secondary Current Distribution interfaces) to control what species are participating in the double-layer charging — that is, the mass exchange between the double layer and the electrolyte outside the double layer.

Perforated Electrode Surface

The Perforated Electrode Surface is applicable to internal boundaries of an electrolyte domains.The node may be used to model a thin and highly conductive perforated (mesh) electrode, immersed in an electrolyte.

Apart from the applicable selection, the node is identical to the Electrode Surface node.

Internal Electrode Surface

The **Internal Electrode Surface** node defines the electrochemical electrode-electrolyte interface between an electrode domain and the electrolyte domain. Use this node as a parent node for Electrode Reactions and the Double-Layer Capacitance of an electrolyte-electrode interface when you explicitly model the electron conducting electrode as a domain in your model.
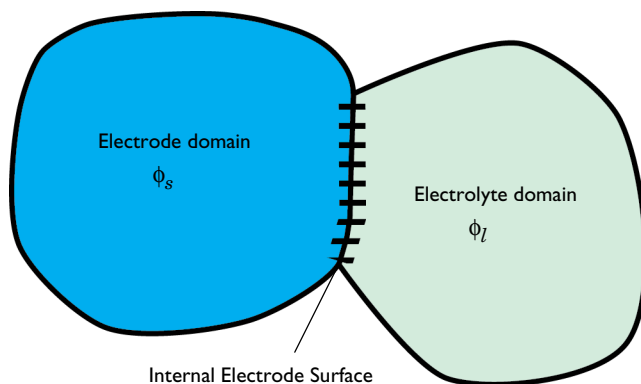
The node can be applied at interior boundaries between electrode and electrolyte domains, and to external boundaries of porous electrode domains. Note that, due to the high conductivity of many electrode materials, an Current Conductor domain can many times be replaced an external condition at the electrolyte boundary. For such cases, consider using the Electrode Surface instead.

For a description of the Film Resistance, Dissolving-Depositing Species and Constraint Settings sections, see the Electrode Surface node.

Q	• Electrode Reactions Theory

Electrolyte Potential

Add the **Electrolyte Potential** node from **Electrolyte** submenus for boundaries, edges, and points to set a fixed potential at a position in the electrolyte. This node can be used to model half-cells, or to set the electrolyte potential at the position of, for example, a reference electrode.

The node sets the potential in the electrolyte, ϕ_l, to be equal to the **Boundary electrolyte potential**, $\phi_{l,\,bnd}$ (SI unit: V).

By right-clicking this node you may add a Harmonic Perturbation subnode.

CONSTRAINT SETTINGS

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

Electrolyte Current

The **Electrolyte Current** boundary condition sets the total current or average current density of a boundary. The condition sets the total inward current without imposing the current density distribution. It will set a constant electrolyte potential along the given boundary, that satisfies the current value setting.

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.

CONSTRAINT SETTINGS

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

🔍	• Electrolyte Current Theory

Electrolyte Current Density

Use the **Electrolyte Current Density** node to specify the current density distribution along a boundary.

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 Electrode Current node instead.

By right-clicking this node you may enable **Harmonic Perturbation**. This means that the node will only be active when solving for Frequency Domain study steps (typically used in AC Impedance studies). The frequency spectrum is specified in the study node.

Thin Electrode Layer

The **Thin Electrode Layer** node can be used to model a thin insulating or resistive sheet, located on an interior boundary in an electrode domain. The node can be used as an alternative to drawing the actual layer domain in the model geometry, which may significantly reduce meshing and solver time, especially in 3D models.

A thin electrode layer can be used to model, for instance, a contact impedance between two electronic conductors.

The layer may be set to be either **Insulating** or **Resistive**.

For the case of **Resistive**, the **Surface Resistance** can either be set directly, or calculated from **Thickness and Conductivity** values.

ADVANCED SETTINGS

Enable **Slit electrolyte potential in porous electrodes** to make the layer fully insulating for the electrolyte phase potential along the selected boundaries.

Electrode-Electrolyte Boundary Interface

Note that this is an advanced physics feature that is normally not used. To display this feature in the context menu, click the **Show More Options** button (👁) and then select **Advanced Physics Options** in the **Show More Options** dialog box. Then add the **Electrode-Electrolyte Boundary Interface** node from the **Electrode** or **Pairs>Electrode** submenu.

Use this node to model an electrochemical interface between an electrolyte and an electrode where the electrolyte domain is not included explicitly in the model. The node can only be applied on outer boundaries to electrode domains. Set the potential of the electrolyte either explicitly, or specify a current condition that the potential of the electrode shall fulfill.

Electrode Reaction and Double-Layer Capacitance subnodes are available from the context menu (right-click the parent node) or from the **Physics** toolbar, **Attributes** menu.

This node is available for the Secondary Current Distribution and Tertiary Current Distribution, Nernst–Planck interfaces.

BOUNDARY CONDITION

This section specifies the potential of the electrolyte phase for the electrolyte-electrode interface. The electrolyte potential is used (via the overpotential) by the **Electrode Reaction** subnodes.

The **Electrolyte potential** will set the potential value directly, whereas **Total current** or **Average current density** both add an extra global degree of freedom for the potential in the electrolyte phase, set to comply with the chosen condition.

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.

Electric Ground

This node to sets the electric potential to zero.

The node is typically used to ground the voltage at an external boundary in a model that contains either electrode or porous electrode domains.

CONTACT RESISTANCE

Enabling **Include contact resistance** allows for a **Contact resistance** R_c (SI unit: $\Omega \cdot m^2$) to be specified and the following current density condition is used:

$$-\mathbf{n} \cdot \mathbf{i}_s = \frac{-\phi_s}{R_c}$$

CONSTRAINT SETTINGS

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

Electric Potential

This node sets the electric potential in the electrode (or a porous electrode), ϕ_s, to a value, $\phi_{s,\,bnd}$ according to the following:

$$\phi_s = \phi_{s,\,bnd}$$

The node is typically used to set the cell voltage at an external boundary in a model that contains either electrode or porous electrode domains.

CONTACT RESISTANCE

Enabling **Include contact resistance** allows for a **Contact resistance** R_c (SI unit: $\Omega \cdot m^2$) to be specified and the following current density condition is used:

$$-\mathbf{n} \cdot \mathbf{i}_s = \frac{\phi_{s,\,bnd} - \phi_s}{R_c}$$

By right-clicking this node you may add a Harmonic Perturbation subnode.

CONSTRAINT SETTINGS

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

Electrode Current Density

The **Electrode Current Density** boundary condition can be applied at an external boundary of a model that contains either electrode or porous electrode domains.

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 Electrode Current node instead.

By right-clicking this node you may enable **Harmonic Perturbation**. This means that the node will only be active when solving for Frequency Domain study steps (typically used in AC Impedance studies). The frequency spectrum is specified in the study node.

Electrode Current

Use the **Electrode Current** node to set the total current or average current density over an external electrode or porous electrode boundary — typically at the interface between the electrode and the current collector or current feeder. The condition sets the total inward current without imposing the current density distribution. The potential along the boundary is calculated in order to satisfy the total value of the current.

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.

CONTACT RESISTANCE

Enabling **Include contact resistance** allows for a **Contact resistance** R_c (SI unit: $\Omega \cdot m^2$) to be specified.

CONSTRAINT SETTINGS

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

Q | • Electrode Current Theory

Electrode Power

The **Electrode Power** boundary condition sets the power drawn from, or inserted to, an electrical cell at external electrode boundary.

When using the **Total power** 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.

CONTACT RESISTANCE

Enabling **Include contact resistance** allows for a **Contact resistance** R_c (SI unit: $\Omega \cdot m^2$) to be specified.

Q | Electrode Power Theory

Harmonic Perturbation

Use the **Harmonic Perturbation** subnode to specify the voltage amplitude perturbation in the frequency domain. The harmonic perturbation is only applied when solving for a Frequency Domain study type, which is typically used in AC Impedance studies.

The **Harmonic Perturbation** subnode can be added to the Electric Potential, Electrolyte Potential. The subnode is available from the context menu (right-click the parent node) or from the **Physics** toolbar in the **Contextual** group.

The frequency spectrum is specified in the study node.

You may also specify harmonic perturbations to the Electrode Current Density, Electrolyte Current Density and Electrode Surface nodes.

Electrode Potential

Use the **Electrode Potential** node to set a boundary condition for the electric potential with respect to a defined reference potential.

Electric potentials defined by the Electric Reference Potential and Reference Electrode point nodes can be used as input when specifying the **Electric reference potential** $\phi_{vs,ref}$ (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.

External Short

Use the **External Short** node to connect two electrodes over an external connector with a given **Resistance** R (SI unit: ohm).

The boundary selected in the External Short node will be set to a constant potential, $\phi_{s,here}$, and the integrated current over the boundary will be computed according to Ohm's law:

$$\phi_s = \phi_{s,\,here}$$

$$\phi_{s,\,here}: \int_{d\Omega} (\mathbf{n} \cdot \mathbf{I}_s)\mathrm{d}d\Omega = -\frac{\phi_{s,\,here} - \phi_{s,\,there}}{R}$$

where $\phi_{s,there}$ (V) is the potential of the connected electrode. Use the **Connected Potential** list to choose among available connection potentials for the value of $\phi_{s,there}$.

Initial Values for Adsorbing-Desorbing Species

The node sets the initial values for the surface coverage of adsorbing-desorbing species dependent variables.

This node is available as a subnode for the Electrode Surface, Perforated Electrode Surface and Internal Electrode Surface. The node is not available if no adsorbing-desorbing species are present in the parent node.

Initial Values for Dissolving-Depositing Species

The node sets the initial values for the dissolving-depositing surface concentrations dependent variables.

This node is available as a subnode for the Internal Electrode Surface and Electrode-Electrolyte Boundary Interface. The node is not available if no dissolving-depositing species are present or if the **Solve for dissolving-depositing species concentrations** check box is cleared in the parent node.

Nonfaradaic Reactions

Use the **Nonfaradaic Reactions** node to define the reaction rate for dissolving-depositing species due to nonfaradaic (not electrochemical) reactions that occur on the boundary.

This node is available as a subnode to an Electrode Surface if there are dissolving-depositing species present in the parent node.

Reference Electrode

The **Reference Electrode** node is a point feature applicable to electrolyte domains. It defines a global electric reference potential and can be used in the Electrode Potential node for setting the electric potential of an electrode boundary with respect to the reference potential.

EQUILIBRIUM POTENTIAL
See Electrode Reaction for information about the settings of this section.

🔍	Electrode Potentials and Reference Electrodes

Electric Reference Potential

The **Electric Reference Potential** node is a point feature applicable to electrode domains. It defines a global electric reference potential equal to the electric potential in the point and can be used in the Electrode Potential feature for setting the electric potential of an electrode boundary with respect to the reference potential.

	Electrode Potentials and Reference Electrodes

Circuit Terminal

This feature is only available with an AC/DC Module or a Battery Design Module license.

Use the **Circuit Terminal** node to specify a coupling to the **External I vs U** node in the **Electrical Circuit** interface.

The Electrode, Shell Interface

The **Electrode, Shell (els)** interface ( ), found under the **Electrochemistry** branch ( ) when adding a physics interface, models electric current conduction in the tangential direction on a boundary.

The physics interface is suitable for modeling thin electrodes where the potential variation in the normal direction to the electrode is negligible. This assumption allows for the thin electrode domain to be replaced by a partial differential equation formulation on the boundary. In this way the problem size can be reduced, and potential problems with mesh anisotropy in the thin layer can be avoided.

Ohm's law is used in combination with a charge balance to describe the conduction of currents in the shell electrode.

When this physics interface is added, these default nodes are also added to the **Model Builder** — **Electrode**, **Electric Insulation** (the default edge or point condition), and **Initial Values**. Then, from the **Physics** toolbar, add other nodes that implement, for example, edge or point conditions and current sources. You can also right-click **Electrode, Shell** 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 `els`.

THICKNESS

Ω	For 2D components, enter a value or expression for the **Out-of-plane thickness** d (SI unit: m). The default value is 1 m.

The dependent variable (field variable) is for the **Electric potential**. The name can be changed but the names of fields and dependent variables must be unique within a model.

DISCRETIZATION

To see all settings in this section, click the **Show More Options** button (👁) and select **Advanced Physics Options** in the **Show More Options** dialog box.

🔍	• Theory for the Electrode, Shell Interface • Boundary, Edge, Point, and Pair Nodes for the Electrode, Shell 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.

Boundary, Edge, Point, and Pair Nodes for the Electrode, Shell Interface

The Electrode, Shell 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 physics nodes are described in this section:

- Boundary Current Source
- Current Source
- Electrode
- Electric Insulation

- Electric Potential
- External Current Density
- Ground
- Initial Values
- Normal Current Density

These nodes are available and described for the Current Distribution interfaces, where edges (3D components) or points (2D and 2D axisymmetric components) are selected instead of boundaries.

- Electrode Potential
- Electric Reference Potential

	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.

	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.

Electrode

The **Electrode** node defines the current conduction in the tangential plane. Use the node to define the electrode thickness and electrical conductivity.

ELECTRODE

The **Electrode thickness** s (SI unit: m) defaults to 10^{-14} m.

The default **Electrical conductivity** σ (SI unit: S/m) uses values **From material**. Or select **User defined**. For **User defined** enter values or expressions for an isotropic or anisotropic conductivity. Select **Isotropic**, **Diagonal**, **Symmetric**, or **Full** depending on the properties

of the electrolyte. To use another type of temperature dependence than a linear temperature relation, enter any expression for the conductivity as a function of temperature. Then enter a value or expression in the field or matrix.

ⓠ   Theory for the Electrode, Shell Interface

Initial Values

The **Initial Values** node adds the electric potential that can serve as an initial guess for a nonlinear solver. If more than one initial value is needed, add **Initial Values** nodes from the **Physics** toolbar.

INITIAL VALUES

Enter values or expressions for the **Electric potential** (SI unit: V). The default value is 0 V.

External Current Density

Use the **External Current Density** node to define the external current density.

EXTERNAL CURRENT DENSITY

Based on space dimension, enter the vector components (**x**, **y**, and **z** for 3D components, **x** and **y** for 2D, or **r** and **z** for 2D axisymmetric components) of the **External current density i_e** (SI unit: A/m^2). The defaults are $0 A/m^2$.

Current Source

The **Current Source** node adds a source term to Equation 4-7. Use this node to define the current source.

ELECTRODE CURRENT SOURCE

Enter a value or expression for the **Current source Q_i** (SI unit: A/m^3). The default is $0 A/m^3$.

Normal Current Density

The **Normal Current Density** node is applicable to exterior boundaries that represent either a source or a sink of current. It sets a condition for the current density according to:

$$\nabla_T \cdot \mathbf{i}_s = i_n$$

The node can be used to couple the Electrode, Shell interface to the electrode reactions in an Electrochemistry interface that describes the electrolyte currents in the adjacent domain.

NORMAL CURRENT DENSITY

Enter a value for the **Electrode current source** i_n (SI unit: A/m^2). The default is 0 A/m^2.

Electric Insulation

The **Electric Insulation** node is the default edge (3D components) and point (2D and 2D axisymmetric components) condition and describes the edges of the shell (boundary) that do not conduct electricity.

Boundary Current Source

The **Boundary Current Source** node is available on edges (3D components) and points (2D and 2D axisymmetric components) and sets a condition for the current density according to:

$$\mathbf{i}_s \cdot \mathbf{n} = i_{s,\,0}$$

BOUNDARY CURRENT SOURCE

Enter a value or expression for the **Inward current density** $i_{s,0}$ (SI unit: A/m^2). The default is 0 A/m^2.

Ground

The **Ground** node is available on edges (3D components) and points (all components) and sets the potential according to $\phi_s = 0$.

> ⚠️ Beware that constraining the potential on edges or points in 3D or on points in 2D usually yields a current outflow that is mesh dependent.

CONSTRAINT SETTINGS

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

Electric Potential

The **Electric Potential** node is available on edges (3D components) and points (all components) and sets the potential according to $\phi_s = \phi_{s,0}$.

EDGE OR POINT SELECTION

> ⚠️ Beware that constraining the potential on edges or points in 3D or on points in 2D usually yields a current outflow that is mesh dependent.

ELECTRIC POTENTIAL

Enter the value or expression for the **Electric potential** $\phi_{s,0}$ (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.

The Electroanalysis Model Wizard Entry

The **Electroanalysis (tcd)** (🖊) model wizard entry, found under the **Electrochemistry** branch (🧪) adds a **Tertiary Current Distribution, Nernst–Planck interface** to the model with the **Electrolyte Charge Conservation Model** set to **Electroanalysis** by default.

The Electroanalysis option is suitable for modeling mass transport of diluted species in electrolytes using the diffusion-convection equation, solving for electroactive species concentrations.

The Tertiary Current Distribution, Nernst–Planck Interface also features options for modeling cyclic voltammetry and electrochemical impedance spectroscopy.

Use this model wizard entry to model electroanalytical problems with electrolyte solutions containing a large quantity of inert "supporting" electrolyte. Ohmic loss is assumed to be negligible.

The model wizard entry is available in 1D, 2D, and 3D as well as for axisymmetric components in 1D and 2D.

The default dependent variables are the molar concentrations, `c1` and `c2`, of the two electroactive species in a redox couple and the electric potential, `phis`, which is solved for either in the Electrode or Porous Electrode domain feature.

🔍	• The Tertiary Current Distribution, Nernst–Planck Interface
	• Introduction to Electrochemistry Modeling
	• Theory for Electroanalysis

Theory for the Current Distribution Interfaces

In this section:

> 📝 This theory is also relevant to the Current Distribution on Edges, BEM interface. However, due to the use of BEM, current source terms in the electrolyte, and porous electrodes, cannot be used in this interface.

The Nernst–Planck Equations

The general mass balance for the diluted species in an electrolyte is described by the following equations for each species i:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{N}_i = R_{i,\text{tot}}$$

where $\mathbf{N}_i$ is the total flux of species i (SI unit: mol/(m^2·s)). The flux in an electrolyte is described by the Nernst–Planck equations and accounts for the flux of charged solute

species (ions) by diffusion, migration, and convection; these are respectively the first, second, and third term on right side in the equation below.

$$\mathbf{N}_i = -D_i\nabla c_i - z_i u_{m,i}Fc_i\nabla\phi_l + c_i\mathbf{u} = \mathbf{J}_i + c_i\mathbf{u}$$

where

- c_i represents the concentration of the ion i (SI unit: mol/m^3),
- z_i its valence,
- D_i the diffusion coefficient (SI unit: m^2/s),
- $u_{m,i}$ its mobility (SI unit: s·mol/kg),
- F denotes the Faraday constant (SI unit: C/mol),
- ϕ_l the electrolyte potential,
- $\mathbf{u}$ is, the velocity vector (SI unit: m/s), and
- $\mathbf{J}_i$ denotes the molar flux relative to the convective transport.

$$\mathbf{J}_i = -D_i\nabla c_i - z_i u_{m,i}Fc_i\nabla\phi_l \qquad\qquad (4\text{-}2)$$

The net current density can be described using the sum of all species fluxes:

$$\mathbf{i}_l = F\sum z_i\mathbf{N}_i$$

where $\mathbf{i}_l$ denotes the current density vector (SI unit: A/m^2) in the electrolyte.

Domain Equations for Primary and Secondary Current Distributions

Assuming electroneutrality (which cancels out the convection term) and negligible concentration gradients of the current-carrying ion (which cancels out the diffusion term), the following expression is left for the current density vector in an electrolyte:

$$\mathbf{i}_l = -F^2\sum z_i^2 u_{m,i}c_i\nabla\phi_l\,.$$

Further, assuming approximately constant composition of charge carriers, we can define a constant electrolyte conductivity as:

$$\sigma_l = F^2\sum z_i^2 u_{m,i}c_i$$

the current density in the electrolyte can be written as

$$\mathbf{i}_l = -\sigma_l \nabla \phi_l$$

This equation takes the same form as Ohm's law; in an electrolyte, charge transport is ohmic, subject to the above assumptions.

Conservation of charge yields the domain equation usually used for the electrolyte in the Primary and Secondary Current Distribution interfaces:

$$\nabla \cdot \mathbf{i}_l = 0$$

In a pore electrolyte, the homogenization used in the theory for porous electrodes introduces a source or sink term in the pore electrolyte current balances due to the charge transfer reactions at the electrode-electrolyte interface within the porous material. In such cases, a source term, Q_l, is introduced on the right-hand side of the equation above.

The Primary and Secondary Current Distribution interfaces define two dependent variables: one for the potential in the electrolyte and one for the electric potential in the electrode. The conduction of current in the electrolyte is assumed to take place through transport of ions as described above, while electrons conduct the current in the electrode.

Since Ohm's law is also used for current conduction in the solid electrode phase, the general equation in these interfaces is according to the following:

$$\nabla \cdot \mathbf{i}_k = Q_k$$

with

$$\mathbf{i}_k = -\sigma_k \nabla \phi_k$$

where Q_k denotes a general source term, k denotes an index that is l for the *electrolyte* or s for the *electrode*, σ_k denotes the conductivity (SI unit: S/m) and ϕ_k the potential (SI unit: V).

Electrochemical Reactions and the Difference Between a Primary and a Secondary Current Distribution

Both the primary and secondary current distribution models assume an electrolyte that conducts current according to Ohm's law, with a constant conductivity. The difference between a primary and a secondary current distribution lies in the description of the

electrochemical *charge transfer reaction* at the interface between an electrolyte and an electrode. The charge transfer reactions can be defined as boundary conditions, or as sources or sinks in a domain for the case of *porous electrodes*.

The rate of the electrochemical reactions can be described by relating the reaction rate to the activation *overpotential*. For an electrode reaction, with index m, the activation overpotential, denoted η_m, is the following:

$$\eta_m = \phi_s - \phi_l - E_{eq,m}$$

where $E_{eq,m}$ denotes the *equilibrium potential* (also known as a reduction potential) for reaction m.

In the Primary Current Distribution interface, the electrochemical reactions are assumed to be fast enough that their kinetics have negligible influence on the cell voltage. Consequently, the activation overpotential, η_m, in this physics interface is equal to zero, and the difference in potential between the electrode and the electrolyte is always equal to the equilibrium potential, $E_{eq,m}$. This condition is implemented as the following constraint on boundaries between electrodes and electrolyte domains:

$$\phi_l = \phi_s - E_{eq,m}$$

A good modeling practice is to estimate the influence of finite reaction kinetics on the cell voltage and to compare the associated activation losses to the ohmic losses in a cell to check the validity of the primary current distribution assumption.

In the Secondary Current Distribution interface, the electrochemical reactions are described as a function of the overpotential. The physics interface uses several relations for the charge transfer current density and the overpotential, such as Butler–Volmer and Tafel expressions. The most general expression is of Butler–Volmer type:

$$i_{loc,m} = i_{0,m}\left(\exp\left(\frac{\alpha_{a,m}F\eta_m}{RT}\right) - \exp\left(\frac{-\alpha_{c,m}F\eta_m}{RT}\right)\right)$$

where $i_{loc,m}$ denotes the local charge transfer current density for reaction m, $i_{0,m}$ the exchange current density, $\alpha_{a,m}$ the anodic transfer coefficient, $\alpha_{c,m}$ the cathodic charge transfer coefficient, F *Faraday's constant*, and R the universal gas constant.

> Both the exchange current density and the overpotential are typically concentration dependent. It is possible include the dependence of kinetics on concentration in the expression above. It also possible to use other kinetics expressions.
>
> See Equilibrium Potentials and the Nernst Equation and Electrode Kinetics Expressions.

The sum of all electrode reaction currents is implemented as a current density condition on the boundary between an electrode and an electrolyte domain according to:

$$\mathbf{i}_l \cdot \mathbf{n} = \sum_m i_{loc, m}$$

$$\mathbf{i}_s \cdot \mathbf{n} = -\sum_m i_{loc, m}$$

Both the Primary Current Distribution and Secondary Current Density Distribution interfaces allow for a domain definition for porous electrodes. For the Primary Current Distribution interface, the same constraint as above is applied.

In porous electrodes for the Secondary Current Distribution interface, the sum of all reaction currents appears as a source in the domain equations:

$$\nabla \cdot \mathbf{i}_l = \sum_m A_{v, m} i_{loc, m}$$

$$\nabla \cdot \mathbf{i}_s = -\sum_m A_{v, m} i_{loc, m}$$

where $A_{v,m}$ is the surface area.

> The only reason to add Porous Electrode descriptions to the Primary Current Distribution interface is to be able to expand a model to include charge transfer resistance.

Domain Equations for Tertiary Current Distributions Using the
Nernst–Planck Equations and Electroneutrality

The domain equations can be derived by starting with The Nernst–Planck Equations. The material balance equation for each species i in the electrolyte is given by the continuity equation, with a flux given by the Nernst–Planck equation:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (\mathbf{J}_i + c_i \mathbf{u}) = R_{i,\,tot}$$

where

- c_i denotes the concentration of species i (SI unit: mol/ m^3),
- $\mathbf{u}$ is, the velocity vector (SI unit: m/s), and
- $\mathbf{J}_i$ denotes the molar flux relative to the convective transport(see Equation 4-2)

The material balances give one equation per unknown species concentration.

> The concentration gradients are not assumed to be negligible here, and so the contribution of ion diffusion to overall current density can be nonzero. (Compare with the Domain Equations for Primary and Secondary Current Distributions.)

There is one more unknown dependent in the variable, the *electrolyte potential*, which requires an additional equation to close the system. This equation is the electroneutrality condition, which follows from dimensional analysis of Gauss's law. In a typical electrolyte solution, it is accurate over lengths greater than a few nanometers:

$$\sum z_i c_i = 0$$

Using the electroneutrality condition reduces the number of dependent concentration variables by one.

Further, by combining the electroneutrality condition with the sum of all species flux vectors and the species mass balance equation, multiplied by the individual species charges, results in expressions for the current vector and a current balance equation, respectively.

The expression for the current density in the electrolyte, $\mathbf{i}_l$, reads:

$$\mathbf{i}_l \ = \ F\sum_{i=1}^{n} z_i(-D_i\nabla c_i - z_i u_{m,i} F c_i \nabla \phi_l) \ = \ F\sum_{i=1}^{n} z_i \mathbf{J}_i$$

whereas current balance in the electrolyte, used for solving for the electrolyte potential, then becomes:

$$\nabla \cdot \mathbf{i}_l = \ Q_l$$

where Q_l can here be any source or sink. (Q_l is typically nonzero for porous electrodes). These formulations are also valid for the pore electrolyte in porous electrodes, except for the transport properties that have to be corrected for porosity and tortuosity. In such cases, the source or sink, Q_l, denotes the charge transfer reactions in the porous electrode and/or the nonfaradaic source or sink due to double layer charge and discharge.

The charge transfer reaction can be parameterized by arbitrary functions of the concentrations of the species in the redox couple and the local electric and electrolyte potentials. The most common way to describe the reaction kinetics is to use a Butler–Volmer expression for the charge transfer current density. See The Butler–Volmer Equation.

In the current balance in a porous electrode, the local current density multiplied by the specific surface area of an electrode gives a contribution to the source or sink, Q_l, due to electrochemical reactions.

Mass Fluxes and Sources Due to Electrochemical Reactions

When relating the species fluxes at an electrode surface to the electrical currents, the general electrochemical reaction formula:
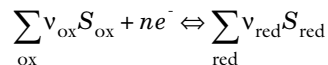
$$\sum_{ox} v_{ox} S_{ox} + n e^{-} \Leftrightarrow \sum_{red} v_{red} S_{red}$$

is used to define the stoichiometric coefficients, v_i, with v_i being positive (v_{red}) for products and negative (v_{ox}) for the reactants in a reduction reaction. The number of participating electrons, n, is always positive.

The molar species fluxes, N_i (SI unit: mol/(m^2·s)), perpendicular to an electrode-electrolyte interface are calculated by summing all the flux contributions from the electrode reactions of index m, according to Faraday's laws:

$$N_i = \sum_m \frac{\nu_{i,m} i_{\text{loc},m}}{n_m F}$$

where $i_{\text{loc},m}$ is the local current density (SI unit: A/m^2) of the electrochemical reaction, n_m the number of participating electrons and F (SI unit: C/mol) is the *Faraday constant*. Note that $i_{\text{loc},m}$ denotes the current density perpendicular to the electrode surface.

The molar species flux, N_i, is obtained from the normal component of the molar species flux vector over the electrode-electrolyte interface:

$$N_i = \mathbf{N}_i \cdot \mathbf{n}$$

where $\mathbf{n}$ is the normal vector of the boundary pointing into the domain.

For a porous electrode, the electrochemical reactions result in species source terms calculated from:

$$R_{i,\,\text{molar}} = -\sum_m a_{v,m} \frac{\nu_{i,m} i_{loc,m}}{n_m F}$$

where $a_{v,m}$ (SI unit: m^2/m^3) is the specific surface area.

Deposition-Dissolution Rates, Growth Velocities, and Thicknesses on an Electrode Surface

The rate of dissolution or deposition on due to an electrode reaction is defined based on the reaction stoichiometry, $\nu_{i,m}$, and the local current density, $i_{\text{loc},m}$, as described in Mass Fluxes and Sources Due to Electrochemical Reactions.

If the reaction rate is known, the total growth $v_{\text{dep, tot}}$ (m/s) is defined as the sum of the velocity contributions for all species and electrode reactions according to:

$$v_{\text{dep, tot}} = -\sum_i \frac{M_i}{\rho_i} \sum_m \frac{\nu_{i,m} i_{\text{loc},m}}{n_m F} \tag{4-3}$$

Where M_i (SI unit: kg/mol) is the molar mass and ρ_i (SI unit: kg/m^3) the density of the species. (i is the species index, and m the index of the electrode reaction).

This velocity may be used in deforming geometry models as a boundary condition for the geometry deformation by assuming that dissolution or deposition always occurs in

the normal direction to an electrode boundary, with the velocity being directed into the electrolyte domain:

$$\frac{\partial \mathbf{x}}{\partial t} \cdot \mathbf{n} = v_{\text{dep, tot}}$$

In a time-dependent simulation one may also introduce a surface concentration variable, $c_{s,i}$ (mol/m^2) on the boundary and calculate the accumulated surface concentration change by using a local ordinary differential equation (ODE):

$$\frac{dc_{s,i}}{dt} = -\sum_m \frac{\nu_{i,m} i_{\text{loc},m}}{n_m F}$$

The total deposited thickness s_{tot}(m) can then be defined as

$$s_{\text{tot}} = \sum_i \frac{M_i}{\rho_i} c_{s,i}.$$

Stoichiometric Coefficients for Double Layer Capacitive Charging

A negative capacitive current corresponds to the accumulation of negative charge on the electrode surface, and a corresponding counterbalanced positive charge accumulating in the double layer. This can be understood in terms of conservation of current: cathodic capacitive current at the electrode corresponds to the overall injection of negative charge (from the double layer) into the electrolyte, just as a cathodic Faradaic current would add negative charge to the electrolyte through electron transfer.

Consider an overall reaction as:

$$2e^-(\text{electrical circuit}) + A^+(\text{solution}) + X^-(\text{double layer})$$
$$\Rightarrow$$
$$2e^-(\text{electrode surface}) + A^+(\text{double layer}) + X^-(\text{solution})$$
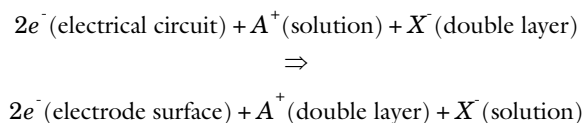
This corresponds to a negative charge of $2F$ being moved from double layer to solution. Following the convention that the reaction is written in the order of cathodic current (as above), then with respect to the free solution species, the cation is a reactant (negative stoichiometry) and the anion is a product (positive stoichiometry). This suggests $\nu_A = -1$, $\nu_X = +1$, and $n = 2$ for an ideal double layer where both anion and cation have similar contributions to the double layer charge.

Film Resistance

If a resistive film forms on the interface between an electrode and an electrolyte, this results in additional potential losses. To model a film resistance, an extra dependent variable for the potential drop over the film, $\Delta\phi_{s,\text{film}}$, is introduced. The governing equation is:

$$\Delta\phi_{s,\text{film}} = i_{\text{tot}}R_{\text{film}}$$

Where R_{film} (SI unit: ohm·m^2) is a generalized film resistance and i_{tot} the sum of all currents over the interface. The activation overpotentials, η_m, for all occurring electrode reactions on the electrode with the film receive an extra potential contribution due to the film resistance according to:

$$\eta_m = \phi_s - \Delta\phi_{s,\text{film}} - \phi_l - E_{0,m}$$

If the thickness and conductivity of the film are known, the resistance can be written as:

$$R_{\text{film}} = \frac{s_0 + \Delta s}{\sigma_{\text{film}}}$$

where s_0 is the reference/initial film thickness, Δs the electrode thickness change, and σ_{film} the conductivity (SI unit: S/m) of the film.

Equilibrium Potentials and the Nernst Equation

Consider an arbitrary, possibly multi-electron step, redox reaction involving a number of species S_i defined as

$$\sum_{i:\nu_i < 0} |\nu_i|S_i + ne^- \leftrightarrow \sum_{i:\nu_i > 0} |\nu_i|S_i$$
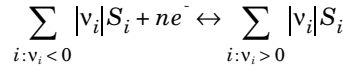
where ν_i is the stoichiometric coefficient of the reacting species of index i and n is the number of participating electrons.

The equilibrium potential of the electrode reaction, E_{eq} (V), is the electrode potential (the difference between the electrode phase and electrolyte phase potentials, $\phi_s - \phi_l$) for which the net reaction rate (and the local current density, i_{loc}) is zero.

The equilibrium potential is directly related to the change of Gibbs free energy of the reacting species, ΔG, as

$$E_{eq} = -\frac{\Delta G}{nF}$$

Since the free energy of the reacting species is concentration dependent, also the equilibrium potential is concentration (activity) dependent. E_{eq} is usually defined according to the Nernst equation as

$$E_{eq} = E_{eq,\,ref} - \frac{RT}{nF} \ln \prod_i \left(\frac{a_i}{a_{i,\,ref}}\right)^{\nu_i}$$

where $E_{eq,\,ref}$ (V) is the equilibrium potential for a reference state for which all species activities a_i (unitless) are equal to a chosen set of reference activities $a_{i,\,ref}$ (unitless).

For ideal solutions, the activities are replaced by concentrations. Standard conditions correspond to reference concentrations of 1M for soluble species in the electrolyte, partial pressures of 1 atm for gaseous species. Constant activities of 1 is used for solid (metal) species and solvents.

Electrode Kinetics Expressions

A number of different analytical expressions for the current density perpendicular to the electrode surface, $i_{loc,m}$, are available. In the following paragraphs, the index m is dropped. All parameters are understood to refer to a specific reaction.

THE EQUILIBRIUM POTENTIAL AND THE OVERPOTENTIAL

The rate of the electrochemical reactions can be described by relating the reaction rate to the activation overpotential. For an electrode reaction, the activation overpotential, denoted η (V), is the following:

$$\eta = \phi_s - \phi_l - E_{eq}$$

where E_{eq} denotes the equilibrium potential.

THE BUTLER–VOLMER EQUATION

A common expression for the current density as a function of the activation overpotential, in modeling of electrochemical systems, is the Butler–Volmer equation:

$$i_{loc} = i_0 \left(\exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right)$$

where α_c (unitless) denotes the cathodic charge transfer coefficient, α_a (unitless) the anodic charge transfer coefficient, and i_0 (SI unit: A/m^2) is the exchange current density.

It should be noted that, although used extensively for all sorts of reactions in the electrochemical community, the Butler–Volmer equation was originally derived for single-electron transfer reactions (for instance implying that the reaction does not involve the breaking or creation of a chemical bond).

Concentration Dependence and the Exchange Current Density
The exchange current density is generally concentration dependent. For certain conditions, it is possible to derive analytical expressions for i_0. Assuming a concentration dependent equilibrium potential defined by the Nernst equation (see previous section Equilibrium Potentials and the Nernst Equation), the kinetics to follow the law of mass action, and the condition that $\alpha_a + \alpha_c = n$, then the exchange current density becomes as follows:

$$i_0 = i_{0,\,\mathrm{ref}} \prod_{i:\nu_i > 0} \left(\frac{a_i}{a_{i,\,\mathrm{ref}}} \right)^{\frac{\alpha_c \nu_i}{n}} \prod_{i:\nu_i < 0} \left(\frac{a_i}{a_{i,\,\mathrm{ref}}} \right)^{\frac{-\alpha_a \nu_i}{n}}$$

where $i_{0,\,\mathrm{ref}}$ is the exchange current density (SI unit: A/m^2) at the reference state. The above expression can be derived from the mass action law, which gives the following expression for the local current density:

$$i_{\mathrm{loc}} = i_{0,\,\mathrm{ref}} \left(\prod_{i:\nu_i > 0} \left(\frac{a_i}{a_{i,\,\mathrm{ref}}} \right)^{\nu_i} \exp\left(\frac{\alpha_a F \eta_{\mathrm{ref}}}{RT} \right) - \prod_{i:\nu_i < 0} \left(\frac{a_i}{a_{i,\,\mathrm{ref}}} \right)^{-\nu_i} \exp\left(\frac{-\alpha_c F \eta_{\mathrm{ref}}}{RT} \right) \right)$$

where the overpotential η_{ref} (SI unit: V) is measured using relative to a reference state, which yields:

$$\eta_{\mathrm{ref}} = \phi_s - \phi_l - E_{\mathrm{eq,\,ref}}.$$

This latter form of the Butler–Volmer equation, where the reference overpotential and the exchange current density do not vary with concentration, is usually preferable numerically.

The law of mass action is usually not suitable for defining complex reactions involving multiple electron steps. For certain multi-electron reactions, where one electron transfer step is rate limiting, it is possible to derive a lumped Butler–Volmer expressions using the following relation for the exchange current density (see Ref. 1):

$$i_0 = i_{0,\,\mathrm{ref}} \prod_i \left(\frac{a_i}{a_{i,\,\mathrm{ref}}}\right)^{\gamma_i}$$

where γ_i are generic exponential coefficients. For this case, α_a and α_c may be independently defined. By rearranging the Butler–Volmer expression using η_{ref} similarly to what was done for the mass action law case above, the γ_i coefficients relate to the anodic, $\xi_{a,i}$, or cathodic, $\xi_{c,i}$, reaction orders according to

$$\xi_{a,\,i} = \gamma_i + \frac{\alpha_a \nu_i}{n}$$

and

$$\xi_{c,\,i} = \gamma_i - \frac{\alpha_c \nu_i}{n}\,.$$

Exchange Current Density and Rate Constants

In electroanalysis, one commonly defines electrode kinetics in terms of rate constants rather than exchange current densities.

For instance, for a one electron redox couple of concentrations c_o and c_r, with the same reference concentration c_{ref} for both species, and $i_{0,\,\mathrm{ref}} = k_0 F c_{\mathrm{ref}}$, the mass action law expression above can be rewritten as

$$i_{\mathrm{loc}} = k_0 F\left(c_r \exp\left(\frac{\alpha_a F \eta}{RT}\right) - c_o \exp\left(\frac{-\alpha_c F \eta}{RT}\right)\right)$$

where k_0 (m/s) is the heterogeneous rate constant.

Generic Concentration Dependent Butler–Volmer Type Kinetics

This expression type gives more freedom for the user to define concentration dependent Butler–Volmer types of expressions, where the anodic and cathodic terms of the current density expression, typically depending on the local concentrations of the electroactive species at the electrode surface, may be individually defined:

$$i_{\mathrm{loc}} = i_0\left(C_{\mathrm{R}} \exp\left(\frac{\alpha_a F \eta}{RT}\right) - C_{\mathrm{O}} \exp\left(\frac{-\alpha_c F \eta}{RT}\right)\right)$$

Here C_{R} and C_{O} are dimensionless expressions, describing the dependence on the reduced and oxidized species in the reaction. Note that if $C_{\mathrm{O}} \neq C_{\mathrm{R}}$ when $\eta = 0$, this kinetics expression results in $i_{\mathrm{loc}} \neq 0$, thus violating the concept of equilibrium. This

may result in thermodynamical inconsistencies, for instance when coupling an electrochemical model to heat transfer.

SIMPLIFICATIONS OF THE BUTLER–VOLMER EQUATION

Linearized Butler–Volmer

The charge transfer reaction can be expressed by a linearized Butler–Volmer expression, which can be used for small overpotentials ($\eta \ll RT/F$) and is usually referred to as the low-field approximation. This approximation gives the following linearized equation:

$$i_{\text{loc}} = i_0 \left(\frac{(\alpha_a + \alpha_c)F}{RT} \right) \eta$$

Anodic and Cathodic Tafel Equations

By assuming either high anodic or cathodic overpotentials for a given current (that is, slow kinetics or low i_0), one of the terms in the original Butler–Volmer potentials can be neglected.

The anodic Tafel equation is implemented as follows:

$$i_{\text{loc}} = i_0 \cdot 10^{\eta/A_a}$$

where A_a (SI unit: V) is the so-called Tafel slope. A_a relates to the corresponding transfer coefficient as follows

$$A_a = \frac{RT \ln 10}{\alpha_a F}$$

The cathodic Tafel expression is defined according to:

$$i_{\text{loc}} = -i_0 \cdot 10^{\eta/A_c}$$

where the sign accounts for the negative cathodic charge transfer current. Here, A_c is required to be negative and relates to the transfer coefficient according to

$$A_c = -\frac{RT \ln 10}{\alpha_c F}$$

LIMITING CURRENT DENSITY

The steady-state rate of electrode reactions can never exceed the rate at which reactants and products can be transported to and from the electrode surface. When explicitly including mass transport in a model, this dependence is typically described in concentration dependence of the equilibrium potential and the exchange current density as described above.

When not explicitly including mass transfer in the domain equations one can still include the effect of transport limitations by the assumption of a Nernst diffusion layer at the electrode surface, and a first-order dependence between the charge transfer current and the local concentration of a reacting species, resulting in the following kinetics expression:

$$i_{loc} = \frac{i_{expr}}{1 + \left\| \frac{i_{expr}}{i_{lim}} \right\|}$$

where i_{expr} (A/m^2) is the current density expression in the absence of mass transport limitations for the species, and i_{lim} (A/m^2) is the limiting current density that corresponds to the maximum transport rate of the species. The derivation of this expression assumes high overpotentials so that either the anodic or a cathodic term in the Butler–Volmer equation may be neglected.

LINEARIZE CONCENTRATION DEPENDENCE FOR LOW CONCENTRATIONS

Consider a concentration-based kinetic expression

$$\frac{dc}{dt} = r = -kc^{\nu}$$

where ν and k are positive numbers and the desired behavior is that the rate r and the concentration c should equal zero in the converged solution at infinite time. However, if c, due to numerical fluctuations in the solver process, becomes negative during iterating, issues may arise.

First consider the case when ν equals 1 (or any odd positive integer). Negative values of c will then cause the rate to become positive, resulting in a "self-stabilizing" situation where c will be approaching 0 with time.

A second case to consider is when ν is an even integer larger than 1. The rate then will become increasingly negative for negative values of c, resulting in an "exploding" solution, iterating c toward minus infinity. The standard solution for these cases, which

also works for noninteger ν values larger than 1, is to change the expression c in the rate term to $\max(c,eps)$, where eps is a small number. This will avoid the "exploding" behavior, but result in poor convergence rate for negative c values since the Jacobian of the rate with respect to c then becomes zero for negative c values.

The third case is when ν is a noninteger between 0 and 1. Note now that Jacobian with respect to c of the rate expression now contains $c^{\nu-1}$, which will approach minus infinity when c approaches zero from the positive side. This may result in poor convergence, and the $\max()$ wrapping will not improve convergence in this case.

The solution for the third case is to linearize the concentration dependence for low concentrations; that is, to use

$$r = -kc^{\nu} \qquad c > c_{\mathrm{lim}}$$

$$r = -kcc_{\mathrm{lim}}^{\nu-1} \qquad c <= c_{\mathrm{lim}}$$

which results in the desired convergence behavior for low and negative concentrations. Note, however, that the linearization may result in thermodynamic inconsistencies so that, for instance, relations like the Nernst equation for the equilibrium potential are no longer fulfilled. The linearization may also improve convergence of the second case above.

Theory for Specific Current Distribution Feature Nodes

ELECTROLYTE THEORY

The Electrolyte node defines a current balance in the electrolyte. The domain equation is:

$$\nabla \cdot \mathbf{i}_l = 0$$

where $\mathbf{i}_l$ denotes the current density vector. In free electrolyte, there is no source or sink of charge.

The definition of the current density vector depends on the equation formulation of the electrolyte charge transport, as discussed above in Domain Equations for Primary

and Secondary Current Distributions and Domain Equations for Tertiary Current Distributions Using the Nernst–Planck Equations and Electroneutrality.

POROUS ELECTRODE THEORY

A porous electrode is a mixed material with one electrode phase and one electrolyte phase. (A special case of a porous electrode is the gas diffusion electrode, as found in a fuel cell. These contain a gas pore phase which is inert to charge transfer.) To model a porous electrode we define two separate current balances according to the following equations:

$$\nabla \cdot \mathbf{i}_l = Q_l \quad \text{and} \quad \nabla \cdot \mathbf{i}_s = Q_s$$

In these equations, $\mathbf{i}_l$ denotes the current density vector in the electrolyte, as discussed above in Domain Equations for Primary and Secondary Current Distributions and Domain Equations for Tertiary Current Distributions Using the Nernst–Planck Equations and Electroneutrality.

In addition to the current balances, it is necessary to also formulate mass balance equations for the species in the electrolyte phase for the tertiary case.

It is also common to used corrected conductivities and diffusion parameter values in a porous electrode to account for the lowered volume fraction of the conducting phase, and the longer transport distance due to the tortuosity of the pores.

The current balances in the pore electrolyte and in the electrode matrix contain sources and sinks according to the charge transfer reactions that take place in the electrode catalyst. For example, if only one charge transfer reaction takes place in the porous electrode, the domain equations are the following:

$$\nabla \cdot \mathbf{i}_l = A_v i_{\text{loc}}$$
$$\nabla \cdot \mathbf{i}_s = -A_v i_{\text{loc}}$$

where A_v denotes the specific surface area (dimension L^2/L^3), and i_{loc} the local current density defines the rate of the charge transfer reactions, for instance according to the Butler–Volmer equation. For various ways of defining i_{loc} see Electrode Kinetics Expressions.

If the porous electrode is a cathode, then the charge transfer reaction is a source for the current balance in the electrode, because it receives current from the pore electrolyte. The charge transfer reaction is then a sink for the current balance in the pore electrolyte, because the current is transferred from the pore electrolyte to the electrode in a cathodic reaction.

The corresponding sources and sinks in the current balances that are due to the charge transfer reactions are also coupled to the material balances for the charged species. This means that the local current density expression above is also included in the material balances as a reaction term, R_i, by using Faraday's laws for each of the species that take part in charge transfer reactions.

🔍   • For the Primary and Secondary Current Distribution interfaces, see .

             • For the Tertiary Current Distribution, Nernst–Planck interface, see .

ELECTRODE REACTIONS THEORY

Charge transfer reactions occurring at an interface between an electrode and an electrolyte domain gives rise to a normal current flux that equals the sum of all reaction currents according to

$$\mathbf{i}_l \cdot \mathbf{n} = \sum_m i_{\text{loc}, m}$$

$$\mathbf{i}_s \cdot \mathbf{n} = -\sum_m i_{\text{loc}, m}$$

where $i_{\text{loc},m}$ (A/m^2) is the current density of the charge transfer electrode reaction of index m, $\mathbf{i}_l$ the current density vector in the electrolyte and $\mathbf{i}_s$ the current density vector in the electrode.

POROUS ELECTRODE REACTIONS THEORY

For a porous electrode, the electrode reaction current densities are multiplied by the surface area to yield a source or sink in the current balance domain equation according to:

$$\nabla \cdot \mathbf{i}_l = \sum_m A_v i_{\text{loc},m}$$

$$\nabla \cdot \mathbf{i}_s = -\sum_m A_v i_{\text{loc},m}$$

where A_v is the specific surface area of the electrocatalyst.

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ELECTRODE THEORY

Electron conduction in an is modeled using Ohm's law. The domain equation is the following:

$$\nabla \cdot \mathbf{i}_s = 0$$

where $\mathbf{i}_s$ denotes the current density vector according to:

$$\mathbf{i}_s = -\sigma_s \nabla \phi_s$$

and where σ_s denotes the electrical conductivity and ϕ_s the potential of the electron conducting (metal) phase.

ELECTROLYTE CURRENT DENSITY THEORY

An applied current density can be defined as its component perpendicular to the boundary according to:

$$\mathbf{i}_l \cdot \mathbf{n} = i_{n,l}$$

The current density can also be defined including all its components:

$$\mathbf{i}_l = \mathbf{i}_{l,\text{bnd}}$$

where $\mathbf{i}_{l,\text{bnd}}$ is a given expression for the current density vector.

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ELECTROLYTE CURRENT THEORY

The boundary condition sets the total current at a given position in the electrolyte without imposing a current density distribution. The conditions yields a constant electrolyte potential, along the given boundary, that satisfies the total value of the current. The boundary condition is a good choice in the middle of a cell with planar electrodes, where the isopotential level can be a plane (or close to a plane in 3D, or line in 2D) but where the current density distribution is unknown.

The feature adds one unknown variable, the electrolyte potential, $\phi_{l,\,\text{bnd}}$, along the boundary. It then adds one additional equation for the total current, which is an integral over the boundary:

$$\int_{\partial\Omega} \mathbf{i}_l \cdot \mathbf{n}\,ds \,=\, I_{n,\,l}$$

The average current density condition imposes the same equation but multiplies the current density by the area of the boundary to obtain the value of the total current $I_{n,\,l}$.

ELECTRODE CURRENT THEORY

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$$\int_{\partial\Omega} \mathbf{i}_s \cdot \mathbf{n}\,ds \,=\, I_{n,\,s}$$

where

$$\mathbf{i}_s \,=\, -\sigma_s \nabla \phi_s$$

and σ_s denotes the electrode conductivity and ϕ_s the electric potential. The average current density condition imposes the same equation but multiplies the current density by the area of the boundary to obtain the value of the total current, $I_{n,s}$.

If a contact resistance R_c is included, the following current density condition is used:

$$-\mathbf{n} \cdot \mathbf{i}_s \,=\, \frac{\phi_{s,\,\text{bnd}} - \phi_s}{R_c}$$

SYMMETRY THEORY

The boundary condition, in the Primary Current Distribution and Secondary Current Distribution interfaces is identical to the Insulation condition and is expressed according to the equation below.

$$\mathbf{i}_k \cdot \mathbf{n} = 0$$

where $\mathbf{i}_k$ denotes the current density vector and $k = l$, s is an index for the electrolyte and electrode, respectively.

The Symmetry boundary condition for the Tertiary Current Distribution, Nernst–Planck interface imposes a no-flux condition for the molar flux of species at a boundary. The condition is expressed as follows:

$$\mathbf{J}_i \cdot \mathbf{n} = 0$$

ELECTRODE CURRENT DENSITY THEORY

An applied can be defined as its component perpendicular to the boundary according to:

$$\mathbf{i}_s \cdot \mathbf{n} = i_{n,s}$$

where

$$\mathbf{i}_s = -\sigma_s \nabla \phi_s$$

and σ_s denotes the electrode conductivity and ϕ_s the electric potential.

The current density can also be defined including all its components:

$$\mathbf{i}_s = \mathbf{i}_{s,\text{bnd}}$$

where $\mathbf{i}_{s,\text{bnd}}$ is a given expression for the current density vector.

ELECTRODE POWER THEORY

The Electrode Power boundary condition is used to specify either the total electrode power or the average electrode power density drawn from or inserted into an electrochemical cell at an electrode boundary.

For a total power condition, the boundary electric potential of an electrode is set to a potential $\phi_{s,\text{bnd}}$, defined by the condition for the total power on the boundary $\partial\Omega$ according to:

$$\phi_s = \phi_{s,\,bnd} \qquad \text{on } \partial\Omega$$

$$\int_{\partial\Omega} (\phi_{s,\,bnd} - \phi_{s,\,ground})(\mathbf{i}_s \cdot \mathbf{n})dS = P_{total}$$

where $\phi_{s,\,ground}$ is the ground potential of the cell, and P_{total} (W) is the power to be drawn.

If a contact resistance R_c is included, the following current density condition is used:

$$-\mathbf{n} \cdot \mathbf{i}_s = \frac{\phi_{s,\,bnd} - \phi_s}{R_c}$$

For an average power condition, P_{total} is calculated by:

$$P_{total} = P_{avg}A$$

where P_{avg} is the average power density on the boundary, and A is the boundary area.

For a galvanic cell, such as a battery during discharge or a fuel cell, there is a maximum power level, beyond which a further current increase causes a lowered output power due to increasing voltage losses. A result of this is that there can be two existing solutions for the same power setting. In these cases the choice of initial values determines the final solution.

Electrode Power

ION EXCHANGE MEMBRANE THEORY

Ion-exchange membranes typically contain a polymer matrix with a number of fixed ionic groups.

Since these charges are fixed, there is no need to explicitly model the transport of these charges, but when calculating the sum of charges, used in the Nernst–Planck (with electroneutrality) or the Nernst–Planck–Poisson set of equations, one need to add this fixed space charge.

For Nernst Planck with electroneutrality, the electroneutrality condition reads

$$\rho_{fix} + F\sum z_i c_i = 0$$

For the Nernst–Planck–Poisson case, the total space charge density becomes

$$\rho_v \;=\; \rho_{\text{fix}} + F\sum z_i c_i$$

ION EXCHANGE MEMBRANE BOUNDARY THEORY

The electrochemical potential μ_i of a charged species of index i is

$$\mu_i \;=\; RT\ln a_i + \phi_l z_i F$$

where $T(\text{K})$ is the temperature, R (mol/(J K)) the molar gas constant, a_i is the species activity, ϕ_l is the electrolyte potential, z_i the species charge, and F(C/mol) is Faraday's constant.

At equilibrium the electrochemical potentials on each side of the free electrolyte - ion-exchange membrane interface are equal.

Setting the species activity to equal the concentration and denoting the liquid electrolyte phase and an ion-exchange membrane phases as 1 and 2, respectively, the Donnan potential, $\Delta\phi$ (V), describes the relation between the concentration of a species, c_i (mol/m3), at each side of the boundary and the electrolyte potentials:

$$\Delta\phi_l \;=\; \phi_{l,\,1} - \phi_{l,\,2} \;=\; -\frac{RT}{z_i F}\ln\!\left(\frac{c_{i,\,1}}{c_{i,\,2}}\right)$$

which may be rearranged to

$$c_{i,\,2} \;=\; c_{i,\,2}\exp\!\left(-\frac{z_i F(\phi_{l,\,1} - \phi_{l,\,2})}{RT}\right)$$

The molar flux of each species in the liquid electrolyte is continuous over the membrane-liquid interface

$$\mathbf{n}\cdot\mathbf{J}_{i,\,1} \;=\; \mathbf{n}\cdot\mathbf{J}_{i,\,2}$$

Since the total current density is the sum of all species fluxes, times the individual species charges, the current densities $\mathbf{I}_l$ in the normal direction $\mathbf{n}$ of the membrane-liquid interface boundary is also continuous:

$$\mathbf{n}\cdot\mathbf{I}_{l,\,1} \;=\; \mathbf{n}\cdot\mathbf{I}_{l,\,2}$$

Reference

1. J. O'M. Bockris, A.K.N. Reddy, and M. Gamboa-Aldeco, *Modern Electrochemistry*, vol. 2A, 2nd ed., ch. 7, sec. 7.6, Kluwer Academic/Plenum Press, New York, 2000.

Theory for Electrochemical Heat Sources

Irreversible voltage losses in an electrochemical cell can occur due to the following phenomena:

- Charge transport in the electrolyte (Joule heating)
- Charge transport in the solid conductor materials (Joule heating)
- Activation overpotentials in the electrode reactions
- Heat of mixing

In addition, reversible heat sources and sinks can appear due to the entropy changes in the electrode reactions.

Most Electrochemistry interfaces define and announce heat source variables that can be used by the General Source and the Boundary Heat source nodes in the Heat Transfer interfaces.

An alternative way to couple an electrochemical interface to a heat transfer interface is by the use of the Multiphysics nodes that become available in the model builder tree if there is both a Heat Transfer interface and an Electrochemistry interface available in the same component.

The Electrochemical Heating multiphysics node defines a domain heat source in the heat transfer interface, based on the sum of irreversible (Joule heating and activation losses) and reversible heat in the electrochemistry interface.

You can also use the heat source variables defined by the electrochemistry interfaces when setting up manual heat couplings between different components in a model. For instance if you are using a 1D electrochemical cell model to calculate an average heat source in a 3D heat transfer model. The names of the heat source variables are xxx.Qh (domain, Joule heating and porous electrode reactions) and xxx.Qbfc (boundary, electrode surface reactions), where xxx is the electrochemistry interface identifier.

🔍	• Electrochemistry Interfaces • Multiphysics Coupling Nodes

Joule Heating Due to Charge Transport

As the charged particles are transported in an electric field, electrical energy is converted into heat. The heat source terms for Joule heating in the electrode and electrolyte phases are computed similarly by multiplying the current vector to the gradient of the potential field variable according to

$$Q_{JH} = -(\mathbf{i}_s \cdot \nabla \phi_s + \mathbf{i}_l \cdot \nabla \phi_l) \tag{4-4}$$

Heating Due to Electrochemical Reactions

For an electrochemical reaction process one can write the total heat balance as:

Heat generated = Total Reaction Energy – Electrical Energy Generated

Using Faraday's law for an electrode reaction, m, at the interface between the electron and ion conducting phase this corresponds to

$$Q_m = \left(\frac{\Delta H_m}{n_m F} - \left(\frac{\Delta G_m}{n_m F} - \eta_{m,\,tot} \right) \right) i_m \tag{4-5}$$

where ΔH_m is the enthalpy change of the reaction, and ΔG_m is the Gibbs free energy of the reaction, ΔG_m, defined as

$$\Delta G_m = \Delta H_m - T \Delta S_m$$

where ΔS_m is the net entropy change. Equation 4-5 may now be rearranged into

$$Q_m = \left(\eta_{m,\,tot} + \frac{T \Delta S_m}{n_m F} \right) i_m \tag{4-6}$$

where the first term represents the irreversible activation losses, and the second term is the reversible heat change due to the net change of entropy in the conversion process.

In Equation 4-5 we have used the total overpotential, $\eta_{m,tot}$ (including potential effects from film resistances and similar), defined as

$$\eta_{m,\,tot} = \phi_s - \phi_l - E_{eq,\,m}$$

The equilibrium potential is related to ΔG_m in the following way:

$$E_{\text{eq}, m} = -\frac{\Delta G_m}{n_m F}$$

By the relation between the temperature derivative of the equilibrium potential and the entropy:

$$\frac{\partial E_{\text{eq}, m}}{\partial T} = \frac{\Delta S_m}{n_m F}$$

the local heat source due to the electrochemical conversion process becomes

$$Q_m = \left(\eta_{m, \text{tot}} + T\frac{\partial E_{\text{eq}, m}}{\partial T} \right) i_m$$

Alternatively, by defining the thermoneutral voltage of the reaction as

$$E_{\text{therm}, m} = -\frac{\Delta H_m}{n_m F}$$

one may also define the heat source as

$$Q_m = (\eta_{m, \text{tot}} + (E_{\text{eq}, m} - E_{\text{therm}, m})) i_m$$

The total heat source due to the electrochemical reactions, Q_{EC}, for an electrode surface is the sum of all individual heat sources of the electrode reactions according to

$$Q_{EC} = \sum_m Q_m$$

For a porous electrode joule heating and electrochemical sources are summed up for a total heat source in the domain according to

$$Q_{\text{TOT}, p} = \sum_m a_{v, m} Q_m + Q_{JH}$$

Heating Due to Heat of Mixing

If the enthalpy varies with the local concentration of the reacting species of the reaction, there are also heat of mixing sources associated with the concentration gradients and resulting molecular flux of the reacting species from the bulk to the surface that have to been to included for a correct thermal balance of the cell. The heat

of mixing effects are typically small (zero for ideal gases) and are generally not included in the Electrochemistry interfaces.

Total Overpotential Calculation for Concentration Dependent Kinetics

When using the Concentration Dependent kinetics option, in the Porous Electrode Reaction and Electrode Reaction nodes, the equilibrium potential is typically a constant referring to a reference state, and the concentration dependence of the kinetics is accounted for only in the pre-exponential terms according to

$$i_{\text{loc}, m} = i_{0, m}\left(C_{R, m}\exp\left(\frac{\alpha_{a, m}F\eta_m}{RT}\right) - C_{O, m}\exp\left(\frac{-\alpha_{c, m}F\eta_m}{RT}\right)\right)$$

where

$$\eta_m = \phi_s - \phi_l - E_{\text{eq}, m}$$

A result of this is that, when the pre-exponential factors $C_{O,m}$ and $C_{R,m}$ differ due to concentration gradients, we at zero activation overpotential may have a net charge-transfer current density flowing over the electrode-electrolyte interface. This local current density obviously should give rise to a heat source. The solution is to add a concentration overpotential term to the total overpotential when calculating the heat sources.

When using the Concentration Dependent kinetics option, the overpotential, used in the irreversible heat term above, is calculated as follows:

$$\eta_{m, \text{tot}} = \phi_s - \phi_l - E_{\text{eq}, m} + \eta_{m, \text{conc}}$$

where

$$\eta_{m, \text{conc}} = \frac{RT}{n_m F}\ln\frac{C_{O, m}}{C_{R, m}}$$

If the number of electrons is not available,

$$n_m = \alpha_{\dot{a}, m} + \alpha_{c, m}$$

is assumed.

References

1. Bernardi and others, "A General Energy Balance for Battery Systems," *J. Electrochem. Soc.*, vol. 132, pp. 5–12, 1985.

2. Thomas and others, "Thermal Modeling of Porous Insertion Electrodes," *J. Electrochem. Soc.*, vol. 150, pp. A176–A192, 2003.

3. j. Newman and K.E. Thomas-Alyea, *Electrochemical Systems*, Chapter 13 Thermal Effects, Wiley, 2012.

Theory for the Electrode, Shell Interface

The Electrode, Shell Interface defines electrode current conduction in a thin shell on a boundary. The electrolyte current distribution in the adjacent domain is typically solved for by a separate physics interface.

In this section:

- Governing Equations
- Coupling to Other Physics Interfaces

Governing Equations

The Electrode, Shell interface solves for the electric potential ϕ_s (SI unit: V) on a boundary, using the following governing equation:

$$\nabla_T \cdot (s\mathbf{i}_s) = -i_n \tag{4-7}$$

where ∇_T is the tangential gradient operator, s (SI unit: m) is the electrode layer thickness, and i_n (SI unit: A/m^2) are the sum of all currents flowing out from the electrode (in the normal direction to the boundary). Furthermore, $\mathbf{i}_s$ (SI unit: A/m^2) is the tangential current density vector along the electrode boundary, defined as

$$\mathbf{i}_s = -\nabla_T \sigma_s \phi_s \tag{4-8}$$

where σ_s is the electric conductivity (SI unit: S/m). The next section discusses Coupling to Other Physics Interfaces.

Coupling to Other Physics Interfaces

ELECTRODE POTENTIAL IN OTHER PHYSICS INTERFACES

Typically the boundary electric potential in the Electrode Surface node is set to the electric potential in the Electrode, Shell interface.

ELECTRODE REACTION CURRENTS

The sum of currents can be coupled to other electrochemistry interfaces, calculating i_n as

$$i_n = i_{\text{tot}}$$

where i_{tot} (SI unit: A/m^2) is the sum of all electrode currents in the coupled Electrochemistry interface.

ELECTRODE LAYER THICKNESS

The electrode thickness, s, can typically be coupled to an External Depositing Electrode (External Corroding Electrode) node in the Electrodeposition, Moving Mesh (Corrosion, Moving Mesh) interface, in that case s is calculated as

$$s = s_0 + \Delta s_{\text{tot}} \tag{4-9}$$

where s_0 is the initial electrode layer thickness, and Δs_{tot} is the electrode thickness change, calculated by the coupled Electrochemistry interface.

HEAT SOURCE

The electron conduction gives rise to a Joule heating source Q_H (SI unit: W/m^2) according to

$$Q_H = -s\mathbf{i}_s \cdot \nabla_t \phi_s$$

Theory for Electroanalysis

The theory related to the **Electroanalysis** charge conservation model in The Tertiary Current Distribution, Nernst–Planck Interface (tcd) is described in this section:

- Electroanalytical Methods
- Supporting Electrolyte
- Domain Equations for the Electroanalysis Case
- Electrode Boundary Conditions in the Electroanalysis Model
- The Electroanalytical Butler–Volmer Equation
- Counter Electrodes and Overall Charge Balance

Electroanalytical Methods

Electroanalysis is the science of quantitative electrochemical measurement of the composition or properties of a chemical system. Common electroanalytical methods include: (cyclic) voltammetry, (chrono)amperometry, potentiometry, coulometry, and electrochemical impedance spectroscopy (EIS). These methods are experiments performed either in a static electrolyte solution or in an electrolyte solution subject to a forced fluid flow. The results sought in electroanalysis include:

- Measurement of the concentration of an analyte — for example, glucose, or a gas-phase species that dissolves in the electrolyte solution. This technique is often referred to as *electrochemical sensing*. The most common sensing method is by recording the concentration-dependent current due to an analyte-specific reaction: this is called *amperometric sensing*.
- Measurement of the kinetic and/or thermodynamic parameters describing an electrochemical reaction on a given electrode surface.
- Measurement of the transport properties of an electroactive chemical species.
- Investigation of the mechanism of an electrochemical reaction and the further reactivity of the electrochemically generated chemical species.

Supporting Electrolyte

When performing electroanalytical experiments, it is conventional to add a large quantity of inert salt to the solution — this artificially added salt is called *supporting*

electrolyte. The purpose of the supporting electrolyte is to increase the conductivity of the solution, and hence to eliminate the electric field from the electrolyte.

A negligible electric field provides two advantages for electroanalysis:

- The voltage due to the resistance of the electrolyte when the cell draws current ("ohmic drop") is minimal. Therefore, the potential difference applied across the electrochemical cell is localized at the electrode–electrolyte interfaces, and so the activation overpotential perceived by the redox couple at this interface is almost exactly proportional to the applied cell voltage. The kinetic behavior of the electrochemical cell then has no explicit dependence on the magnitude of the drawn current.

- The contribution of migration to the transport of charged chemical species is negligible compared to the contribution of diffusion (and of convection, in a forced flow). Therefore the transport properties of the system are linearized, and they do not depend on the magnitude of the drawn current.

These properties greatly simplify the design and analysis of electroanalytical experiments. Therefore, the use of a supporting electrolyte is very common in electrochemical sensing and electroanalysis.

The amount of supporting electrolyte required for the assumption of zero electric field to be sound is dependent on the system. Typically it becomes valid when the concentration of inert salt exceeds the concentration of analyte by a factor of 10–100, but this is not always the case.

Even for the conductivities of electrolyte solutions in the presence of excess supporting electrolyte, the electric field is not negligible if significant current density is drawn. Electroanalysis typically draws small currents because the purpose is measurement. In processes where an electrochemical reaction is driven — such as electrolysis, electrodeposition, batteries, and fuel cells — current densities are typically much larger, so that the desired extent of reaction is achieved in a reasonable time. Under these conditions, significant electric fields are likely and other charge conservation models should be used instead of the Electroanalysis option.

Domain Equations for the Electroanalysis Case

The Electroanalysis option assumes that the electric field is zero, and so the electrolyte potential is constant. Since you can arbitrarily choose to ground the electrolyte potential at any point, set it to $\phi_l = 0$.

This is equivalent to the assumption of infinite electrolyte conductivity. Therefore the Electroanalysis option does not solve for charge transfer within domains, because current density is not meaningfully defined within the electrolyte.

The transport of chemical species in an electrolyte solution obeys the Nernst–Planck equation for the flux of species i:

$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_l + c_i \mathbf{u} = \mathbf{J}_i + c_i \mathbf{u}$$

Here $\mathbf{J}_i$ denotes the molar flux relative to the convective transport.

At zero electric field, this reduces to:

$$\mathbf{N}_i = -D_i \nabla c_i + c_i \mathbf{u} \tag{4-10}$$

where the only contributions to the flux of a chemical species are from diffusion and convection respectively. In the absence of convection (no fluid flow, $\mathbf{u} = 0$), this is also known as *Fick's first law of diffusion*:

$$\mathbf{N}_i = \mathbf{J}_i = -D_i \nabla c_i$$

A mass balance also applies to each chemical species:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{N}_i = R_{i,\text{tot}} \tag{4-11}$$

The Electroanalysis charge conservation model solves Equation 4-10 and Equation 4-11 for the unknown concentrations of each chemical species under analysis.

This combination is often written as a single equation for the unknown c_i. For zero convection, zero reaction, and a constant diffusion coefficient, the domain equation is:

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i \tag{4-12}$$

Equation 4-12 is *Fick's second law of diffusion*.

!	The Electroanalysis charge conservation model is not suitable to explicitly model the transport of the supporting electrolyte, since the migration of the supporting electrolyte is always its dominant mode of mass transport. For a coupled model including the chemical species of all charge-carrying species, use the electroneutrality model in Tertiary Current Distribution, Nernst–Planck interface.

💡	You can also include additional chemical species and reactions that are not involved in the electrochemical reaction.

🔍	• Electrode Potentials and Reference Electrodes • The Tertiary Current Distribution, Nernst–Planck Interface

Electrode Boundary Conditions in the Electroanalysis Model

The *activation overpotential* at an electrode–electrolyte interface with respect to the electrode reaction m is defined as:

$$\eta_m = \phi_s - \phi_l - E_{eq, m}$$

This is the potential difference perceived by a redox couple, measured against the equilibrium potential of the couple; it provides the thermodynamic driving force for an electrochemical reaction by faradaic charge transfer between the electrode and the electrolyte domains.

Subject to the approximation of constant electrolyte potential ($\phi_l = 0$), this equation reduces to:

$$\eta_m = \phi_s - E_{eq, m}$$

The activation overpotential is independent of the properties of the adjacent electrolyte. It only depends on the applied electrode potential ϕ_s and the equilibrium potential of the redox couple, where both are measured against a common reference potential.

The current density due to an electrode reaction at a point on an electrode surface is computed using an electrochemical rate expression. For most practical electroanalytical applications, the rate depends on the local concentration which varies during the study, and so the most relevant expression is The Electroanalytical Butler–Volmer Equation.

Ⓠ | Electrode Kinetics Expressions

The flux N_i of the chemical species i (SI unit: mol/m^2) across an electrode surface depends on the current densities i_m associated with the electrode reactions m according to *Faraday's laws of electrolysis*. These can be written as:

$$N_i = \sum_m \frac{v_{i,m} i_m}{n_m F} \qquad (4\text{-}13)$$

where $v_{i,m}$ is the stoichiometric coefficient of species i with respect to reaction m (in the reductive direction), and n_m is the number of transferred electrons. F is the *Faraday constant*, which is the charge on a mole of electrons (96485.3365 C/mol).

The surface flux is applied as a boundary condition:

$$N_i = \mathbf{N}_i \cdot \mathbf{n} \qquad (4\text{-}14)$$

Equation 4-13 and Equation 4-14 constitute the coupling between charge balance and mass balance. This coupling only applies at the electrode–electrolyte interface, which is a boundary to the domain where the electroanalysis charge conservation model solves for chemical species transport.

The total current density is the sum of faradaic (electrode reaction) components and nonfaradaic components (i_{nf}) such as current due to Electrode Kinetics Expressions:

$$i_{total} = \sum_m i_{loc,m} + i_{nf}$$

The experimentally measurable total current I (SI unit: A) drawn at an electrode can be computed by integration of the local current density (SI unit: A/m^2) across the electrode area:

$$I_{\text{total}} = \int_{\partial\Omega} i_{\text{total}} ds$$

The Electroanalytical Butler–Volmer Equation

A one-electron electrochemical reaction between two solution-phase species can be written as a reduction $Ox + e^- \leftrightarrow Red$.

Ox and Red represent the oxidized and reduced forms of the chemical species, respectively.

The most general equation to describe the rate of this reaction as it proceeds at an electrode surface is the electroanalytical *Butler–Volmer equation*:

$$i_{\text{loc}} = k_0 F \left(c_{\text{Red}} \exp\left(\frac{\alpha_a F \eta}{RT} \right) - c_{\text{Ox}} \exp\left(\frac{-\alpha_c F \eta}{RT} \right) \right) \qquad (4\text{-}15)$$

where k_0 is the *heterogeneous rate constant* (SI unit: m/s) and α_c is the (cathodic) transfer coefficient (dimensionless). For a one-electron reduction, the anodic and cathodic transfer coefficients are related as $\alpha_a + \alpha_c = 1$.

When the current is zero, the electroanalytical Butler–Volmer equation can be rearranged to the thermodynamic *Nernst equation* relating the equilibrium concentrations of the reacting species:

$$c_{\text{Red}} = c_{\text{Ox}} \exp\left(\frac{-FE_{\text{eq}}}{RT} \right)$$

Where the flux of the reacting species is negligible compared to the concentration of these species, the concentrations are roughly constant ($c_{\text{Red}} \sim c_{\text{Ox}} \sim c$). This converts Equation 4-15 into the Butler–Volmer equation written in terms of an exchange current density i_0 (SI unit: A/m^2):

$$i_{\text{loc}} = i_0 \left(\exp\left(\frac{\alpha_a F \eta}{RT} \right) - \exp\left(\frac{-\alpha_c F \eta}{RT} \right) \right)$$

The exchange current density i_0 (SI unit: A/m^2) is then related to the heterogeneous rate constant as $i_0 = k_0 F c$.

Counter Electrodes and Overall Charge Balance

The Electroanalysis charge conservation model does not solve explicitly for the electrolyte potential in the domains. This has the implication that an overall charge balance of a modeled cell does not follow naturally as a result of the domain potential equation (as is the case for instance when solving for Ohm's law in the Secondary Current Distribution interface).

In order to model a charge balance of a cell with an arbitrary number of working electrodes and counter electrodes, the solution is to add an extra degree of freedom for the counter electrode potential, $\phi_{s,\,CE}$, and then solve for this potential to fulfill the following current balance over all electrode surfaces:

$$\phi_{s,\,CE}: \quad \int_{electrodes} i_{tot} dS = 0 \tag{4-16}$$

The counter electrode potential is used in the overpotential, η, in the kinetics expression(s) on the counter electrode.

$$\eta_m = \phi_{s,\,CE} - E_{eq,\,m} \tag{4-17}$$

Note that only one counter electrode potential degree of freedom is added in the model, regardless of the number of counter electrodes that are active.

Domain Equations for the Electroanalysis Case

Electrode Potentials and Reference Electrodes

In all the Electrochemistry branch interfaces, the dependent potential variables are ϕ_s (SI unit: V), the electric potential of the electrode phase (the electron conductor, such as metal), and ϕ_l (SI unit: V), the potential of the electrolyte phase (ion conductor).

Typically the kinetics of the electrochemical reactions are defined using the overpotential, η (SI unit: V), defined as

$$\eta = \phi_s - \phi_l - E_{eq} \tag{4-18}$$

where E_{eq} (SI unit: V) is the equilibrium potential. If it is to apply for all overpotentials, a general kinetic expression for an electrode reaction must be set up so that the charge-transfer current over the electrolyte-electrode interface is zero for zero overpotential (equilibrium conditions).

An implication of Equation 4-18 is that it is the potential difference, $\phi_s - \phi_l$, that governs the kinetics, not the absolute individual values of ϕ_s and ϕ_l. A global change in the reference for both potentials has no impact on the electrode kinetics. As a result of this, the potentials have to be "boot-strapped" in a model in some way, typically by making an arbitrary choice of electric ground — for example, on an external boundary — in order to ensure that there is a unique solution to the problem.

In this section:

- Reference Electrodes
- Boundary Conditions Using Reference Electrode Potentials
- Nodes for Handling Electrode Potentials and Reference Electrodes

Reference Electrodes

In experimental electrochemistry, it is common to use *reference electrodes* when controlling current or voltage with a potentiostat. Potential differences in the system are recorded with respect to the equilibrium potential of the redox couple at the reference electrode. A good reference electrode is designed so that no net charge transfer takes place at its electrode-electrolyte interface. Then the overpotential of the reference is zero, so:

$$\phi_{s,\,\text{ref}} = \phi_l + E_{\text{eq, ref}} \tag{4-19}$$

where $\phi_{s,\,\text{ref}}$ (SI unit: V) is the electric potential of the reference electrode and $E_{\text{eq, ref}}$ (SI unit: V) is the equilibrium potential of the reference electrode reaction.

The electric potentials of the electrodes in the electrochemical cell can then be defined with respect to the reference electrode according to:

$$E_{\text{vs ref}} = \phi_s - \phi_{s,\,\text{ref}} \tag{4-20}$$

where $E_{\text{vs ref}}$ (SI unit: V) is the electrode potential versus the reference potential.

It is important to realize that the presence of an ideal reference electrode in the system has no impact on the physics; the only purpose of the reference electrode is to define a stable reference point for the potential levels.

Boundary Conditions Using Reference Electrode Potentials

The set of boundary conditions defined in a model of an electrochemical cell needs to ensure that no current flows through the reference electrode. A constraint for the potential on the actual reference electrode is not suitable in general since it can create unwanted local sources or sinks of current.

When modeling the control of an electrochemical cell by a *potentiostat*, which monitors and controls the potential of an electrodes versus a reference electrode, the electric potential conditions should be applied to the boundaries over which the current flows in the cell. One electrode (the counter electrode) is typically grounded, whereas an electric potential condition is set on all other (working) electrode boundaries according to

$$\phi_{s,\,\text{bnd}} = E_{\text{vs ref}} + \phi_{s,\,\text{ref}} \tag{4-21}$$

where $\phi_{s,\,\text{bnd}}$ (SI unit: V) is the applied electric boundary potential on the electrode.

Nodes for Handling Electrode Potentials and Reference Electrodes

The node is a point feature applicable to electrolyte domains (in all the Electrochemistry interfaces). It defines a global electric reference potential $\phi_{s,\text{ref}}$ (SI unit: V) according to Equation 4-19. The $\phi_{s,\text{ref}}$ can be used in the Electrode Potential feature for setting the electric potential of an electrode boundary with respect to the reference potential. The variable $E_{\text{vs ref}}$ (SI unit: V), according to Equation 4-20, is also defined in all electrode domains.

The node is a point feature applicable to electrode domains (in all the Electrochemistry interfaces). It defines a global electric reference potential $\phi_{s,ref}$ (SI unit: V) equal to the dependent variable ϕ_s (SI unit: V) in the point. The $\phi_{s,ref}$ can be used in the Electrode Potential feature for setting the electric potential of an electrode boundary with respect to the reference potential.

Whenever a $\phi_{s,ref}$ is defined, the variable $E_{vs\,ref}$ (SI unit: V), according to Equation 4-20, is also defined in all electrode domains.

The is a boundary condition feature, applicable to external boundaries of electrode domains (in all the Electrochemistry interfaces). It sets a boundary condition for the electric potential with respect to a defined reference potential according to Equation 4-21. Electric potentials defined by the Electric Reference Potential and Reference Electrode point feature can be used as input when specifying the Electrode Potential feature.

An Electrode Potential alternative in the Boundary Condition settings list is also available for the Electrode Surface node.

The variable $E_{vs\,ref}$ (SI unit: V), according to Equation 4-20, is also defined on these features.

5

Chemical Species Transport Interfaces

This chapter describes the physics interfaces found under the **Chemical Species Transport** branch ( ).

In this chapter:

- The Transport of Diluted Species Interface
- The Transport of Diluted Species in Porous Media Interface
- The Transport of Concentrated Species Interface
- The Transport of Concentrated Species in Porous Media Interface
- The Chemistry Interface
- The Nernst–Planck–Poisson Equations Interface
- The Electrophoretic Transport Interface
- The Surface Reactions Interface
- The Reacting Flow Interfaces
- The Reacting Flow in Porous Media Interfaces
- The Nonisothermal Reacting Flow Multiphysics Interfaces

The theory for all the interfaces is also discussed at the end of the chapter and links are included with the interfaces.

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.

OUT-OF-PLANE THICKNESS

For 2D components, the **Thickness** field (default value: 1 m) defines a parameter for the thickness of the geometry perpendicular to the two-dimensional cross-section. Both constant and varying thicknesses are supported. The value of this parameter is used, among other things, to automatically calculate molar flow rates from the total molar flux.

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. Both constant and varying areas are supported. The value of this parameter is used, among other things, to automatically calculate molar flow rates from the total molar flux. The default is 1 m^2.

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
- 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}. Its 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 selected, 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 selected. 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** ($\equiv_{\times}$) buttons as needed.

Q
- [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.

S E T T I N G S

The rest of the settings are the same as The Transport of Diluted Species Interface.

F U R T H E R   R E A D I N G

⊕	• 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-8212-sorbing-solute-490

Domain, Boundary, and Pair Nodes for the Transport of Diluted Species Interface

has the following domain, boundary, 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).

- To add a node, go to the **Physics** toolbar, no matter what operating system you are using.
- Contextual subnodes (attributes) are available by clicking the parent node in the Model Builder, and then selecting the subnode from the **Attributes** menu.

- Adsorption
- Concentration
- Continuity on Interior Boundaries
- 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
- Out-of-Plane Flux
- Outflow
- Partition Condition
- Periodic Condition
- Point Mass Source
- Porous Matrix
- Porous Medium
- Porous Electrode Coupling
- Reaction Coefficients
- Reactions
- Solid
- Species Properties
- Species Source
- Surface Reactions
- Surface Equilibrium Reaction
- Symmetry
- Thin Diffusion Barrier
- Thin Impermeable Barrier
- Transport Properties
- 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.

Prescribing Conditions on Fluid-Solid Interfaces

Defining conditions on interfaces between different phases, typically a wall in contact with a fluid, it is worthwhile to be careful with how variables in the conditions are evaluated. COMSOL Multiphysics supports that variables are defined differently on adjacent domains (or any other geometry dimension). Evaluating a variable with differing definitions, the mean value is returned on a boundary separating the different domains. The density, pressure, or temperature are examples of variables that may differ in a fluid and a solid. In order to specify on which side a variable is evaluated, the up and down operators (described in the *COMSOL Multiphysics Reference Manual*) can be used.

Species Properties

Use this node to define parameters specific to each of the species. It is available when the **Migration in electric field** check box is selected in the Transport Mechanisms section of the interface.

The node will change its label depending on what inputs are available in the node. If only **Charge** is available, it will be labeled "Species charges".

CHARGE

Enter the charge number z_c (dimensionless, but requires a plus or minus sign) for each species.

ACTIVITY

This section is available when the **Species Activity** combo box is set to **Debye-Hückel** or **User defined**.

If **Debye-Hückel** is selected, enter the ion size number, a_0, for each species. If **User defined** is selected, enter the activity coefficient, f, for each species.

Transport Properties

The settings in this node are dependent on the check boxes selected under Transport Mechanisms in 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.

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/.

| | • *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/ transport-in-an-electrokinetic-valve-603 |

Solid

Use this node to describe diffusion in a solid phase domain. In this feature, the activities of the species are assumed to be ideal.

DIFFUSION

Specify the diffusion coefficients describing the diffusion of each species in the solid.

Enter a value or expression for the **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**, or **Symmetric** that describes the diffusion transport, and then enter the values in the corresponding element (one value for each species).

ADVANCED

This section is only available with the **Advanced Physics Options** selected and when the model contains a split between the material frame and the spatial frame. A split of these frames occurs when using a **Moving Mesh** node or a Structural Mechanics interface like **Solid Mechanics**. In such a model, the reference geometry (the material frame) differs from the deformed geometry (the spatial frame). The diffusive transport of species is solved for on the material frame, but the equation is adjusted for geometry deformations so that species conservation is achieved on the spatial frame. Use the **Diffusion model** to define the frame of reference for the diffusion tensor.

Select **Reference geometry based (Lagrangian)** to specify the diffusion tensor in the undeformed geometry, implying that the diffusion is defined in the material frame

(indicated by coordinates X, Y, Z). This is the preferred setting for an anisotropic diffusion in combination with solid body translation or rotation. Also in general when the diffusion tensor components have been measured in an undeformed geometry.

Select **Deformed geometry based (Eulerian)** to specify the diffusion tensor in the deformed geometry. This means that the diffusion is defined in the spatial frame (indicated by coordinates x, y, z). Use this setting when the diffusion tensor components have been measured in a deformed geometry.

The **Advanced Physics Options** is found in the **Show More Options** dialog box, accessed by clicking the **Show More Options** button (👁).

Note that multiple species are only available for certain COMSOL Multiphysics add-on products. See details: https://www.comsol.com/products/specifications/.

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_i (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 list. 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 in the case of using the volume of a particular phase (applicable when modeling an unsaturated porous medium).

- 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_l. (θ_l equals the porosity (ε_p) on Porous Medium domains).

- For **Gas phase**, the reaction expressions, in mol/(m^3·s), are multiplied by the gas volume fraction $\theta_g = \varepsilon_p - \theta_l$. θ_g equals 0 for Porous Medium domains.

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:

$$-\mathbf{n} \cdot (-D\nabla c - z u_m F c \nabla \phi) = 0$$

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

$$-\mathbf{n} \cdot (-D\nabla c - z u_m F c \nabla \phi + \mathbf{u}c) = 0$$

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: 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 nontrivial 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 More Options** 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 .

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.

When defining conditions on boundaries between different phases, see the section Prescribing Conditions on Fluid-Solid Interfaces.

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:

$$-\mathbf{n} \cdot (-D \nabla c - z u_m F c \nabla \phi) = J_0$$

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.

When defining conditions on boundaries between different phases, see the section Prescribing Conditions on Fluid-Solid Interfaces.

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:

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 relation between the concentration of a solute species in two adjoining 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.

Select **Partition coefficient** from the **Relation** list to prescribe a linear relationship between the concentration on either side of a boundary. For a species concentration c_i, the ratio between the concentration on the upside and on the downside of the boundary ($c_{i,\mathrm{u}}$ and $c_{i,\mathrm{d}}$ respectively) is then defined in terms of a partition coefficient K_i in the manner of

$$K_i = \frac{c_{i,\,\mathrm{u}}}{c_{i,\,\mathrm{d}}}$$

Use the associated input field to prescribe the partition coefficient for each species.

Select **User defined** from the **Relation** list to set up a nonlinear relation between the up and downside concentrations. For such relations $f(c_i)_u = f(c_i)_d$, where $f(c_i)_u$ is the expression enforced on the upside. Use the associated input fields to enter the upside and downside expressions for each species.

The up and downside of the selected boundary is indicated with a red arrow in the Graphics window. The arrow points from the downside into the upside. Select the **Reverse direction** check box to reverse the direction of the arrow on the selected boundary, and update the definition of the up and downside concentrations accordingly.

| ! | 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. |

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.

BOUNDARY SELECTION

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.

DESTINATION SELECTION

For more complex geometries, it might be necessary to specify the destination selection manually. To do so, right-click the **Periodic Condition** node and choose **Manual**

Destination Selection. You can then specify the boundaries that constitute the destination surfaces in the **Destination Selection** section.

CONSTRAINT SETTINGS

To display this section, click the **Show More Options** button (☞) and select **Advanced Physics Options** in the **Show More Options** dialog box. This section contains settings for specifying the type of constraint and whether to use a pointwise or weak constraint. See Constraint Settings for more information.

ORIENTATION OF SOURCE

To display this section, click the **Show More Options** button (☞) and select **Advanced Physics Options** in the **Show More Options** dialog box. For information about the **Orientation of Source** section, see Orientation of Source and Destination.

ORIENTATION OF DESTINATION

This section appears if the setting for **Transform to intermediate map** in the **Orientation of Source** section is changed from the default value, **Automatic**, and **Advanced Physics Options** is selected in the **Show More Options** dialog box. For information about the **Orientation of Destination** section, see Orientation of Source and Destination.

MAPPING BETWEEN SOURCE AND DESTINATION

To display this section, click the **Show More Options** button (☞) and select **Advanced Physics Options** in the **Show More Options** dialog box. For information about the **Mapping Between Source and Destination** section, see Mapping Between Source and Destination.

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.

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.

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 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: 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 v_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.

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 list.

When defining conditions on boundaries between different phases, see the section Prescribing Conditions on Fluid-Solid Interfaces.

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.

When defining conditions on boundaries between different phases, see the section Prescribing Conditions on Fluid-Solid Interfaces.

> ⚠️ 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.

When defining conditions on boundaries between different phases, see the section Prescribing Conditions on Fluid-Solid Interfaces.

> ⚠️ 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 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 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 the 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, 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 a porous medium. It is used as a subnode to 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** $D_{F,i}$ 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 $\tau_{F,i}$ (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

$$\varepsilon_p = 1 - \sum_i \theta_{s,i} - \sum_i \theta_{\mathrm{imf},i}$$

where $\theta_{s,i}$ 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 in 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, 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 $d\theta/dt$ (SI unit: 1/s).

- For **Time change in pressure head**, enter dH_p/dt (SI unit: m/s) and a **Specific moisture capacity** C_m (SI unit: 1/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** $D_{L,i}$ 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**:

$$c_P = c_{Pmax} \frac{K_L c}{1 + K_L c} \quad , \quad K_P = \frac{\partial c_P}{\partial c} = \frac{K_L c_{Pmax}}{(1 + K_L c)^2}$$

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**:

$$c_P = K_F\left(\frac{c}{c_{ref}}\right)^N \quad , \quad K_P = \frac{\partial c_P}{\partial c} = N\frac{c_P}{c}$$

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

$$K_P = \frac{\partial c_P}{\partial c} = c_{Pmax}b_T(1 + (b_T c)^{N_T})^{-\left(1 + \frac{1}{N_T}\right)}$$

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

$$K_P = \frac{\partial c_P}{\partial c} = \frac{K_B c_0 c_S((K_B - 1)c^2 + c_S^2)}{(c - c_S)^2(c_S + (K_B - 1)c)^2}$$

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** enter an **Adsorption isotherm** $c_{P,c}$ (SI unit: mol/kg):

$$c_P = f(c)$$

For more information, see in the theory section.

FURTHER READING

See the theory chapter in the section .

Volatilization

This feature is available when the **Mass transfer in porous media** check box is selected in 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.

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.

Out-of-Plane Flux

The out-of-plane flux node is used to prescribe a flux in an out-of-plane domain, and it can be used to reduce a model geometry to 2D, or even 1D, when the concentration variation is small in one or more directions. This could be the case for example when the object to model is thin or slender. Figure 5-1 shows examples of possible situations in which this type of geometry reduction can be applied.
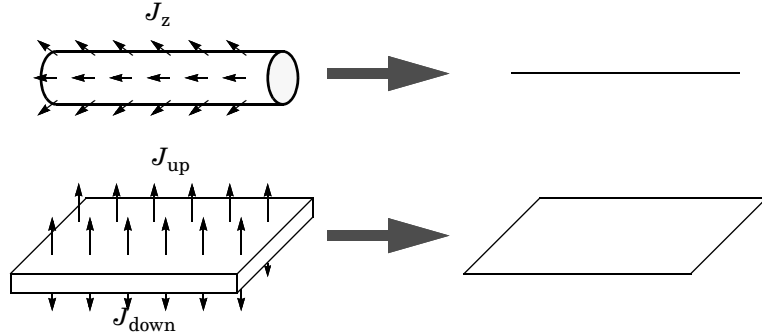
Figure 5-1: Geometry reduction from 3D to 1D (top) and from 3D to 2D (bottom).

For a 1D component this node adds a single out-of-plane molar flux $J_{0,z,i}$ for species i. For a 2D component two fluxes can be prescribed for each species; $J_{0,u,i}$ for the upside of the domain, and $J_{0,d,i}$ for the downside of the domain.

The fluxes are added as a source contribution to the right-hand side of the transport equation. For example, in 2D components with diffusion, convection, and out-of-plane flux present, the mass transfer of species i is defined by the mass conservation equation

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{J}_i + \mathbf{u} \cdot \nabla c_i = R_i + S_{\text{opf}, i}, \tag{5-1}$$

where $S_{\text{opf},i}$ is the out-of-plane source for species i

$$S_{\text{opf}, i} = \frac{J_{0, i}}{d_z} = \frac{J_{0, u, i} + J_{0, d, i}}{d_z}.$$

For external convection on the upside and the downside of the domain, the out-of-plane flux is

$$J_{0,i} = k_{c, u, i}(c_{b, u, i} - c_i) + k_{c, d, i}(c_{b, d, i} - c_i)$$

where k_c is a mass transfer coefficient and c_b is the bulk concentration, the typical concentration far into the surrounding exterior domain. The prescribed flux, J_0, can include any arbitrary user-specified expressions. It can be a constant or a function of a dependent variable or independent variables.

UPSIDE INWARD FLUX

For 1D components, enter the **cross-sectional perimeter** P_c to get the out-of-plane flux

$$J_{0,i} = P_c J_{0, z, i}.$$

The default value of P_c is the circumference. Either keep the default value, for a circular cross-section shape, or edit the value to get a user-defined shape of the out-of-plane cross-section.

The available flux type options are **General inward flux** and **External convection**. 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.

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.

DOWNSIDE INWARD FLUX

The available options are **General inward flux** and **External convection**. The settings are the same as for the Upside Inward Flux section.

For an example of using the Out-of-Plane Flux node, see this application example:

▥	*Mass Transfer from a Thin Domain*: Application Library path **Chemical_Reaction_Engineering_Module/Tutorials/thin_domain**

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.

The Fracture feature has two default subfeatures — the Fluid (Fracture) subfeature where convection and diffusion are specified and the Fracture Material subfeature where the porosity ε_p is defined.

⚠	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}.

For the **Fracture** boundary condition, there are a number of **Attributes** available which can be accessed either via the **Physics** Ribbon toolbar (for Windows) or by right-clicking on the **Fracture** node. These attributes are identical to the Boundary, Edge, Point, and Pair Nodes for the Transport of Diluted Species in Fractures Interface.

Fluid (Fracture)

Use this node to specify the mass transfer in the mobile fluid solvent filling the pores of a fracture.

It uses the same input options as the Fluid subfeature under the Porous Medium feature. There are further details about the settings.

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.

CONVECTION

If transport by convection is active, the velocity field of the solvent needs to be specified. Select an option from the **Velocity field** list to specify the convective velocity along the fracture. For a consistent model, use a Fracture 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

DIFFUSION

Use this section to specify diffusion coefficients describing the diffusion of each species in the solvent fluid.

	The **Diffusion** settings are similar to those for the diffusion coefficients in the Fluid node under Porous Medium.

Fracture Material

Specify the **Porosity,** ε_p (dimensionless) of the porous matrix. This is by default taken **From material**. Select **From pellet bed densities** to compute the porosity from the (dry bulk) **Bed density** ρ_b and the (single phase) **Pellet density** ρ_{pe} through the relation

$$\varepsilon_p = 1 - \frac{\rho_b}{\rho_{pe}}$$

For **User defined**, enter a value or expression for the porosity.

The Transport of Diluted Species in Fractures Interface

The **Transport of Diluted Species in Fractures (dsf)** interface (![icon]), found under the **Chemical Species Transport** branch (![icon]), 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 the model geometry includes boundaries that should not be included in the mass transfer simulation, remove those from the selection list.

OUT-OF-PLANE THICKNESS

For 2D components, the **Thickness** field (default value: 1 m) defines a parameter for the thickness of the geometry perpendicular to the two-dimensional cross-section. Both constant and varying thicknesses are supported. The value of this parameter is used,

among other things, to automatically calculate molar flow rates from the total molar flux.

TRANSPORT MECHANISMS

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}. Its default value is `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

<table>
<tr>
<td rowspan="4">🔍</td>
<td>• Mass Transport in Fractures in the theory section.</td>
</tr>
<tr>
<td>• Numerical Stabilization in the *COMSOL Multiphysics Reference Manual*.</td>
</tr>
<tr>
<td>• Domain, Boundary, and Pair Nodes for the Transport of Diluted Species Interface</td>
</tr>
<tr>
<td>• 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.</td>
</tr>
</table>

Boundary, Edge, Point, and Pair Nodes for the Transport of Diluted Species in Fractures Interface

The Transport of Diluted Species in Fractures 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).

- Concentration
- Flux
- Fracture
- Inflow
- Initial Values

- No Flux
- Outflow
- Reactions
- Species Source

Furthermore, there are the following attributes to the **Fracture** node

- Adsorption
- Dispersion

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 **Boundary material** is used as The Transport of Diluted Species in Fractures Interface is active on boundaries only. The **Density** ρ of the porous media is needed when modeling adsorption to the surface of the porous matrix. By default the option **From material** is selected.

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). Also activate the check box for the species c_i for which adsorption takes place.

- 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 a **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.

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*.

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 Fracture.

This subfeature is available when the **Convection** check box is selected in 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.

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

$$\mathbf{n} \cdot d_{\mathrm{fr}}(D_e \nabla c) = d_{\mathrm{fr}} N_0$$

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

The available options are **General inward flux** and **External convection**. If the latter is chosen, define a **Mass transfer coefficient** and a **Bulk concentration**. Specify the flux of each species individually. To use another boundary condition for a specific species, make sure that the check box for the mass fraction of that species is unchecked.

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.

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, included with the Chemical Reaction Engineering Module, the reaction rate expressions can be automatically generated and picked up using the drop-down list.

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$^3 \cdot$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.

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:

$$\frac{\partial}{\partial t}(\rho \omega_i) + \nabla \cdot (\rho \omega_i \mathbf{u}) = -\nabla \cdot \mathbf{j}_i + R_i \tag{5-2}$$

Using the continuity equation, the sum of all species equations, the equation can be recast in its nonconservative form:

$$\rho \frac{\partial}{\partial t}(\omega_i) + \rho (\mathbf{u} \cdot \nabla) \omega_i = -\nabla \cdot \mathbf{j}_i + R_i \tag{5-3}$$

This form of the equation is the one used in 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.

OUT-OF-PLANE THICKNESS

For 2D components, the **Thickness** field (default value: 1 m) defines a parameter for the thickness of the geometry perpendicular to the two-dimensional cross-section. Both constant and varying thicknesses are supported. The value of this parameter is used, among other things, to automatically calculate mass flow rates from the total mass flux.

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. Both constant and varying areas are supported. The value of this parameter is used, among other things, to automatically calculate mass flow rates from the total mass flux. The default is 1 m^2.

The Transport of Concentrated Species interface always accounts for transport due to convection and 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.

- 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 domain features are enabled:

- Porous Medium
- Porous Electrode Coupling

Maxwell–Stefan Diffusion Model
When using the **Maxwell–Stefan** diffusion model the relative mass flux vector is

$$\mathbf{j}_i = -\rho \omega_i \sum_{k=1}^{Q} D_{ik} \mathbf{d}_k - \frac{D_i^T}{T} \nabla T$$

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·s)) is the thermal diffusion coefficient.

The diffusional driving force is defined as

$$\mathbf{d}_k = \nabla x_k + \frac{1}{p}\left[(x_k - \omega_k)\nabla p - \rho \omega_k \mathbf{g}_k + \omega_k \sum_{l=1}^{Q} \rho \omega_l \mathbf{g}_l \right] \tag{5-4}$$

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

$$\mathbf{g}_k = -\frac{z_k F}{M_k} \nabla \phi \tag{5-5}$$

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 5-40 (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.

$$\omega_1 = 1 - \sum_{i=2}^{Q} \omega_i \qquad (5\text{-}6)$$

CONSISTENT AND INCONSISTENT STABILIZATION

To display this section, click the **Show** button (👁) and select **Stabilization**.

- Two consistent stabilization methods are available — **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

$$0 \le w_{i,\,\text{reg}} \le 1$$

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 (≡ₓ) 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.

The Transport of Concentrated Species in Porous Media Interface

This interface ( ), found under the **Chemical Species Transport** branch ( ), is used to calculate the chemical composition in a fluid mixture transported through the interstices of a porous media. The interface is the same as the *Transport of Concentrated Species* interface but it has a Porous Medium node added by default. All other features for porous media transport is always available.

This interface is dedicated to analyzing mass transport in porous media where the chemical species may be subjected to convection, diffusion, and migration in an electric field. The interface also includes reaction rate expressions and source terms for modeling chemical reactions in porous media. It is also possible to include regions with free flow.

The main feature of the interface is the **Porous Medium** node which adds the governing equations for the mass fractions of all present species. It has two subnodes, **Fluid** and **Porous Matrix**, which in turn are used to define the physical properties corresponding to each phase, and to prescribe the transport properties. The latter are typically the flow field, and when applicable, the electric field. The **Porous Medium** node supports

the use of a Porous Material for defining phase-specific properties, and for sharing them among different physics interfaces.

When this physics interface is added, the following 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 Concentrated 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.

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
- Fluid
- Flux
- Flux Discontinuity
- Inflow
- Initial Values
- Mass Fraction
- No Flux
- Open Boundary
- Out-of-Plane Flux
- Outflow

- Porous Matrix
- Porous Medium
- Porous Electrode Coupling[1]
- Reaction
- Reaction Coefficients[1]
- Reaction Sources
- Species Properties
- Surface Equilibrium Reaction
- Symmetry
- Thin Impermeable Barrier[1]
- 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.

Prescribing Conditions on Fluid-Solid Interfaces

Defining conditions on interfaces between different phases, typically a wall in contact with a fluid, it is worthwhile to be careful with how variables in the conditions are evaluated. COMSOL Multiphysics supports that variables are defined differently on adjacent domains (or any other geometry dimension). Evaluating a variable with differing definitions, the mean value is returned on a boundary separating the different domains. The density, pressure, or temperature are examples of variables that may differ in a fluid and a solid. In order to specify on which side a variable is evaluated, the up and down operators (described in the *COMSOL Multiphysics Reference Manual*) can be used.

Species Properties

Use this node to define parameters specific to each of the species.

The node will change its label depending on what inputs are available in the node. If only **Molar Mass** is available, it will be labeled "Species Molar Masses".

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.

CHARGE

This section is available when the **Migration in electric field** check box is selected in the Transport Mechanisms section of the interface. Enter the charge number z_w (dimensionless, but requires a plus or minus sign) for each species.

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 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 5-4 (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.

CONVECTION

Select the source of the **Velocity field 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**.

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 $u_{m,c}$ (SI unit: s·mol/kg) and enter one value for each species.

The temperature (if you are using mobilities based on the Nernst–Einstein relation) is taken from the **Model Inputs** section.

Porous Medium

Use this node to model the composition in a gas or liquid mixture as it is transported though the interstices of solid porous medium. In addition to transport due to convection and diffusion, the node contains functionality to include species evolution through reactions in the fluid phase.

Species transport in a porous medium is affected both by properties of the fluid phase as well as properties of the solid matrix. These properties are defined in the Fluid node and the Porous Matrix node respectively. The Porous Medium node supports material properties using a Porous Material node, where properties are defined per phase in a similar manner.

Fluid

Use this node to specify the mass transport in a fluid phase filling the pores of a porous medium. It is used as a subnode to Porous Medium.

MODEL INPUTS

Specify the temperature and pressure in the fluid. 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 5-4 (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.

- When present, select a temperature defined by a Heat Transfer interface in the model. 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.

- When present, select a pressure defined by a Fluid Flow interface present in the model. For example, select **Absolute pressure (spf)** to use the pressure defined in a Laminar Flow interface with spf as the name.

DENSITY

Use this section to define the density of the fluid phase, 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.

CONVECTION

Select the source of the **Velocity field 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 that solves for the velocity of the fluid. For example, select **Velocity field (spf)** to use the velocity field defined by in a Single-Phase Flow, Laminar Flow interface with spf as the Name.

When the interface is used in a reacting flow multiphysics coupling, the velocity is automatically defined and the input is disabled.

DIFFUSION

Specify the species molecular and thermal diffusivities in fluid phase 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:

$$f_e = \frac{\varepsilon_p}{\tau_F} \tag{5-7}$$

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 τ_F. Select either **Isotropic** to define a scalar value, or **Diagonal** or **Symmetric** to define anisotropic tensor values.

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.
- When present, select an electric potential defined by an AC/DC interface that is present in the model. For example, select **Electric potential (ec)** to use the electric field defined 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 $u_{m,w}$ and enter one value for each species.

The temperature (if you are using mobilities based or the Nernst–Einstein relation) is taken from the **Model Inputs** section.

PORE WALL INTERACTIONS

In porous media, it is possible to include **Pore Wall Interactions**. This accounts for species collisions with the surrounding media, that is, the pore walls.

For the **Fick's law** and **Mixture-averaged** diffusion models, the diffusion coefficient D_i^M is corrected with the **Wall diffusion** coefficient D_i^W in the following way

$$D_i^{MW} = \left(\frac{1}{D_i^M} + \frac{1}{D_i^W} \right)^{-1}$$

For the **Maxwell-Stefan** diffusion model, the following term is added to the species force balance

$$\ldots + \frac{x_i}{D_{i,\,\text{eff}}^W} \left(\frac{\mathbf{j}_i}{\omega_i \rho} + \mathbf{u}_W \right) = \mathbf{d}_i$$

For weakly adsorbing gases, the **Knudsen** formula can be applied for computing the wall diffusivities, based on the **Pore diameter** d_{pore} (SI unit: m). For other cases, choose **User defined**.

	For isobaric systems featuring concentration gradients in porous media, concentration gradients may give rise to nonzero fluid velocity as a result of the wall interactions. This effect can be modeled using the **Maxwell-Stefan** diffusion model in combination **Pore Wall Interactions**. For this case the wall velocity variable $\mathbf{u}_W$ (`tcs.uW`) can be used to contribute to the fluid momentum balance (either as a **Contributing Velocity** in **Darcy's law**, or as a **Volume Force** in either the **Brinkman Equations** or **Free and Porous Media Flow, Brinkman** interfaces. The multiphysics **Reacting Flow** nodes incorporates this contribution from $\mathbf{u}_W$ automatically.

Porous Matrix

This node defines the porosity, defined as the volume fraction occupied by a fluid phase, when modeling transport in a 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

$$\varepsilon_p = 1 - \sum_i \theta_{s,i} - \sum_i \theta_{\text{imf},i}$$

where $\theta_{s,i}$ and $\theta_{\text{imf},i}$ are the volume fractions given in **Solid** and **Immobile Fluids** subnodes under the **Porous Material** node.

For **User defined**, enter a value or expression for the porosity.

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. 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.

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, 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 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 ($\omega_{0,\omega1}$ for example)

- **Mole fractions** to enter mole fractions ($x_{0,\omega 1}$ for example)
- **Molar concentrations** (SI unit: mol/m^3) to enter molar concentrations ($c_{0,\omega 1}$ for example)
- **Number densities** (SI unit: 1/m^3) to enter number densities ($n_{0,\omega 1}$ for example)
- **Densities** (SI unit: 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.

When defining conditions on boundaries between different phases, see the section Prescribing Conditions on Fluid-Solid Interfaces.

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

$$-\mathbf{n} \cdot \mathbf{j}_i = j_{0,i} \tag{5-8}$$

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.

When defining conditions on boundaries between different phases, see the section Prescribing Conditions on Fluid-Solid Interfaces.

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

$$j_{0,i} = k_{\omega,i}(\omega_{b,i} - \omega_i) \tag{5-9}$$

where $k_{\omega,i}$ is a mass transfer coefficient and $\omega_{b,i}$ 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.)

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: mol/m^3) to enter molar concentrations ($c_{0,\omega 1}$, for example)

- **Number densities** (SI unit: $1/m^3$) to enter number densities ($n_{0,\omega 1}$, for example)

- **Densities** (SI unit: 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.

Out-of-Plane Flux

The out-of-plane flux node is used to prescribe a flux in an out-of-plane domain, and it can be used to reduce a model geometry to 2D, or even 1D, when the variation of mass fraction is small in one or more directions. This could be the case for example

when the object to model is thin or slender. Figure 5-1shows examples of possible situations in which this type of geometry reduction can be applied.
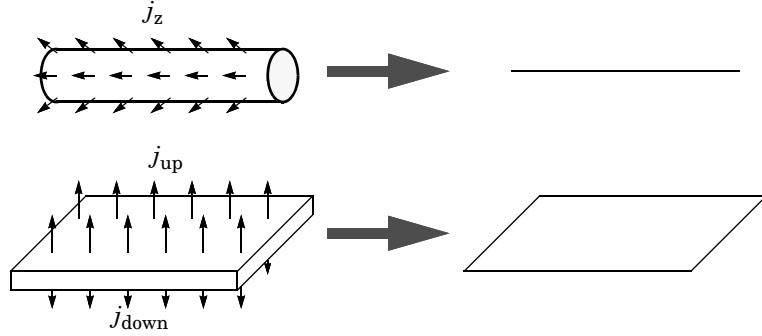
Figure 5-2: Geometry reduction from 3D to 1D (top) and from 3D to 2D (bottom).

For a 1D component this node adds a single out-of-plane mass flux $j_{0,z,i}$ for species i. For a 2D component two fluxes can be prescribed for each species; $j_{0,u,i}$ for the upside of the domain, and $j_{0,d,i}$ for the downside of the domain.

The fluxes are added as a source contribution to the right-hand side of the transport equation. For example, in 2D components with diffusion, convection, and out-of-plane flux present, the mass transfer of species i is defined by the mass conservation equation

$$\rho\frac{\partial}{\partial t}(\omega_i) + \rho(\mathbf{u}\cdot\nabla)\omega_i + \nabla\cdot\mathbf{j}_i = R_i + S_{\text{opf},i},\qquad(5\text{-}10)$$

where $S_{\text{opf},i}$ is the out-of-plane source for species i

$$S_{\text{opf},i} = \frac{j_{0,i}}{d_z} = \frac{j_{0,u,i}+j_{0,d,i}}{d_z}.$$

For external mass transfer on the upside and the downside of the domain, the out-of-plane flux is

$$j_{0,i} = k_{w,u,i}(w_{b,u,i}-w_i) + k_{w,d,i}(w_{b,d,i}-w_i)$$

where $k_{\omega,i}$ is a mass transfer coefficient and $\omega_{b,i}$ is the bulk mass fraction, the typical mass fraction far into the surrounding exterior domain. The prescribed flux, j_0, can include any arbitrary user-specified expressions. It can be a constant or a function of a dependent variable or independent variables.

UPSIDE INWARD FLUX

For 1D components, enter the **cross-sectional perimeter** P_c to get the out-of-plane flux

$$j_{0,i} = P_c j_{0,z,i} \ .$$

The default value of P_c is the circumference. Either keep the default value, for a circular cross-section shape, or edit the value to get a user-defined shape of the out-of-plane cross-section.

The available options are **General inward flux** and **External convection**. Specify the **Inward flux** for each species individually. Select the **Species** check box for the species for which to specify the flux, 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.

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

$$j_{0,i} = k_{\omega,i}(\omega_{b,i} - \omega_i)$$

where $k_{\omega,i}$ is a mass transfer coefficient and $\omega_{b,i}$ is the bulk mass fraction, the typical mass fraction far into the surrounding exterior domain.

DOWNSIDE INWARD FLUX

The available options are **General inward flux** and **External convection**. The settings are the same as for the Upside Inward Flux section.

FURTHER READING

For an example of using the Out-of-Plane Flux node, see this application example:

| | *Mass Transfer from a Thin Domain*: Application Library path **Chemical_Reaction_Engineering_Module/Tutorials/thin_domain** |

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 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:

$$-\mathbf{n} \cdot (\mathbf{N}_d - \mathbf{N}_u) = N_0 \qquad \mathbf{N} = (\rho \omega_i \mathbf{u} + \mathbf{j}_i)$$

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: $kg/(m^2 \cdot s)$) in the corresponding field,

$N_{0, \text{w1}}$ 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 ($\omega_{0,\omega1}$, for example)
- **Mole fractions** to enter mole fractions ($x_{0,\omega1}$, for example)
- **Molar concentrations** (SI unit: mol/m^3) to enter molar concentrations ($c_{0,\omega1}$, for example)
- **Number densities** (SI unit: $1/\text{m}^3$) to enter number densities ($n_{0,\omega1}$, for example) and to describe the number of particles per volume $n = n_0$
- **Densities** (SI unit: kg/m^3) to enter densities ($\rho_{0,\omega1}$, 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

$$K_{\text{eq}} = \frac{\displaystyle\prod_{i \in \text{products}} a_i^{v_i}}{\displaystyle\prod_{i \in \text{reactants}} a_i^{-v_i}}$$

where v_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 v 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 Chemistry Interface

The **Chemistry (chem)** interface ( ) is found under the **Chemical Species Transport** branch ( ) when adding a physics interface.

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.

The following is a description of the features and fields available in 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. Toggle the **Enable electrode reactions** check box to enable the Electrode Potential input in the Model Input section, as well as the Electrode Reaction and Electrode Reaction Group features. 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
Use this setting to define specify what kind of mixture assumption is used. For **Diluted Species** the mixture is composed of low concentration solutes present in a solvent. For **Concentrated Species** a mixture where no single species is considered to be in excess is assumed.

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 molar 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.

SPECIES MATCHING
This section is used to match species solved for in space dependent physics interfaces to the species defined in Chemistry. By doing so the variables for the reaction kinetics and the mixture properties defined by Chemistry can be applied to study chemically reacting or composition dependent systems.

Species Solved For

Use this list to populate the inputs in the **Bulk species** table with dependent variables from a certain mass transfer interface. The **Species solved for** list contains all present interfaces of the **Type** selected in the **Mixture Properties** section. For example, when the **Type** is **Diluted species**, all Transport of Diluted Species interfaces or variants thereof, such as Transport of Diluted Species in Porous Media interface, are available in the list.

Bulk Species

Use the **Bulk species** table to specify the concentrations to be used as arguments in reaction kinetics variables, for example the reaction rate. Reaction kinetics variables are generated by the species features (Species and Species Group) and by the reaction features (Reaction, Electrode Reaction, Reversible Reaction Group, Electrode Reaction Group, and Equilibrium Reaction Group).

The bulk species concentrations are also used in the mixture properties, both for transport properties like the density and viscosity, and thermodynamic properties like the enthalpy or heat capacity.

When a mass transfer interface has been selected in the **Species solved for** list, use the **Molar concentration** column to select one of the dependent variables in the selected interface to the corresponding **Species** in Chemistry. When using a concentrated species interface (defined by the **Type** list in the Mixture Properties section), instead use the **Mass fraction** column to select a dependent variable for each species in Chemistry. For a consistent set up, the species molar mass in the Transport of Concentrated Species interface is updated to the one defined in the Chemistry interface.

The **Molar concentration** and **Mass fraction** columns also includes a **User defined** option, in which case a constant, parameter, or variable expression can be entered in the **Value** column.

Thermodynamics Coupling

When the Thermodynamics is enabled, the species in the Chemistry interface can be coupled 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 Chemistry to a species in the coupled thermodynamic system. For each thermodynamics-coupled species, the required property parameters and functions are added under the corresponding thermodynamic system. When all species are matched, the Chemistry is considered fully coupled and functions representing mixture properties, such as the density, are also added automatically under the same thermodynamic system.

Surface Species

The **Surface Species** table is available when there is at least one surface species (with "(ads)" as suffix).

Specify the concentration of surface species in the table in this section. In addition, if a surface species is present at the same time as an Electrode Reaction, the **Density of sites** input field becomes visible. The **Density of sites** input value will be used as the default reference concentration for surface species reacting in an Electrode Reaction.

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

Solid Species

The **Solid Species** table is available when there is at least one solid species (with "(s)" as suffix).

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

The **Aqueous Species** table is available when there is at least one aqueous species (with "(aq)" as suffix).

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.

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 (selected as default) 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 fit 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

This section is available when the **Thermodynamics** check box is cleared.

Select the **Use activity** check box to solve for species activities instead of species concentrations, which is a common approach when nonideal 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.

CHEMKIN IMPORT FOR SPECIES PROPERTIES

It is available when the **Thermodynamics** check box is cleared.

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.

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]
- Electrode Reaction
- Electrode Reaction Group
- 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 in the **Chemistry** toolbar click **Reaction**.

REACTION FORMULA

Formula
Enter a chemical equation in the **Formula** field. The chemical equation should be of the format "A + B arrow C + D". Here, A and B are reactants, C and D are product species, and arrow denotes a reaction arrow. The participating species should be written with Valid Species Names. Valid reaction arrows are "<=>" for reversible reaction, "=>" for irreversible reaction, and "=" for equilibrium reaction. Species can be given trivial names, or their chemical formulas can be used as names. Examples of valid formulas are; "carbon+oxygen=>carbondioxide", and "C(s)+O2(g)=>CO2(g)".

Click **Apply** to make the interface examine the species taking part in the chemical equation, and automatically add the associated Species features to the Model Builder.

Balance (⚖)
Use the **Balance** button to automatically calculate the stoichiometric coefficients such that the number of atoms of each kind are the same on both sides of the reaction. This turns, for example, the formula "H2+O2=>H2O" into "2H2+O2=>2H2O". The balancing involves parsing all participating species for elements in the periodic table. It

therefore requires that all species in the **Formula** field are written either using their chemical formula, say "H2O", or that each species in the reaction have an enabled **Chemical Formula** field in their **Species** node. For example, it is possible to balance the formula "H2+O2=>water" as long as there is a Species node with the name "water" already present, and an enabled **Chemical Formula**.

For automatic reaction balancing to be successful, requires that the problem is well posed. One example of a problem that is not well posed is "C+H2=>CH4+C2H6", in which case any ratio of CH_4/C_2H_6 could be obtained. Another example is "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:

$$R_i = \sum_j \nu_{ij} r_j \tag{5-11}$$

where ν_{ij} is the stoichiometric coefficient.

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

$$K_{eq} = K_{eq0}$$

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:

$$r_j = k_j^f \prod_{i \in \text{react}} c_i^{-\nu_{ij}} \tag{5-12}$$

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

$$r_j = k_j^f \prod_{i \in \text{react}} c_i^{-\nu_{ij}} - k_j^r \prod_{i \in \text{prod}} c_i^{\nu_{ij}} \tag{5-13}$$

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 species. 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:

$$2\,S_2O_4^{2-} + H_2O \Rightarrow S_2O_3^{2-} + 2\,HSO_3^-$$
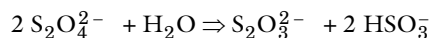
The automatically deduced reaction order is three, however, in the case that water is the solvent, the order should probably be two. This is specified as follows:

Figure 5-3: 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 5-12).

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:

$$k^r = k^f / K_{eq0}$$

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:

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

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:

$$H_j = \sum_{i\,\in\,\text{prod}} \nu_{ij} h_i - \sum_{i\,\in\,\text{react}} (-\nu_{ij}) h_i \tag{5-14}$$

Entropy of Reaction

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

$$S_j = \sum_{i\,\in\,\text{prod}} \nu_{ij} s_i - \sum_{i\,\in\,\text{react}} (-\nu_{ij}) s_i \tag{5-15}$$

In Equation 5-14 and Equation 5-15, 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, v_{ij}, are defined as being negative for reactants and positive for products. Using Equation 5-14 and Equation 5-15 to equate the Gibbs free energy of reaction enables the equilibrium constant to be expressed according to Equation 5-14.

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: in the **Chemistry** toolbar click **Species** or right-click the **Chemistry** node and select it from the context menu.

NAME

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

For a **Species** node added individually, enter a **Name** in the field and click **Apply**. By entering a name consisting of elements from the periodic table, the molar mass is calculated and added in the **Chemical Formula** section. The species charge, and type, are also deduced from the species name.

🔍	Valid Species Names

Select a species type — **Bulk species**, **Surface species**, or **Solvent**. The latter is only available when a diluted solution is assumed. That is when **Type** is set to **Diluted Species** in the **Mixture Properties** section (in the interface level).

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.

C H E M I C A L   F O R M U L A

The **Chemical Formula** section contains the species chemical formula, **Molar mass**, M, and **Charge**, z.

If the name entered for the species consists of only elements from the periodic table, and optionally charge and phase indication, then the **Chemical Formula** field will be populated with the name entered in the **Name** section, and the molar mass and charge will be added to this section. The species molar mass is computed from the mass of occurring individual elements[1]. The rules for writing chemical formulas are the same as those for **Species** names.

🔍 Valid Species Names

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. By entering a chemical formula consisting only of elements from the periodic table (and optionally charge and phase indication), the molar mass, and charge are derived automatically.

When needed, the **Molar mass** can be edited in the corresponding text field. Editing the **Chemical formula** and pressing apply will override the molar mass and charge fields.The **Charge** field cannot be edited as long as a chemical formula is enabled.

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.

With an enabled **Chemical Formula** it is possible to use the trivial name of a species and balance reactions. Having added the Species water, oxygen, and hydrogen, and filled in H2O, O, and H in their respective chemical formula sections, the **Formula** oxygen+hydrogen=water is balanced into oxygen+2hydrogen=water by clicking **Balance** in the **Reaction** node.

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: $mol/(m^3 \cdot s)$), the **Surface rate expression** (SI unit: $mol/(m^2 \cdot s)$), or both. For a bulk species, both expressions appear if surface reactions are present 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.

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: mol/m^3).

CONSTANT CONCENTRATION/ACTIVITY

To account for nonideality 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 activity** check box is selected on the Chemistry interface **Settings** window

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

THERMODYNAMIC EXPRESSIONS

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

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

Electrode Reaction

To add an **Electrode Reaction** node (⚗) either right-click the **Chemistry** node or in the **Chemistry** toolbar click **Electrode Reaction**.

The **Electrode Reaction** subnode defines the electrode kinetics for a charge transfer reaction that occurs on an electrolyte-electrode interface boundary. Use multiple nodes to model multiple reactions, for instance in mixed potential problems.

This node is available with a Battery Design Module, Corrosion Module, Electrochemistry, Module, Electrodeposition Module, or Fuel Cell & Electrolyzer Module license.

REACTION FORMULA

Formula
Enter an electrode reaction Formula, as a reduction reaction. Use the single letter "e" to symbolize an electron. The delimiter between reactants and products has to be written as "<=>" (without quotation marks). The phase of the species, that is (aq) for aqueous dilute ions, (s) for solids, and (g) for gases can be indicated in the name. The phase is used to select an automatic reference state (see Reference Concentrations) for computing the equilibrium potential using the Nernst equation. 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.

EQUILIBRIUM POTENTIAL

The Equilibrium potential, E_{eq} (SI unit: V), is used in the electrode kinetics expressions in the following section (via the definition of the overpotential), or for setting up primary current distribution potential constraints.

Nernst Equation
After providing the reference electrode potential, the equilibrium potential is calculated using the Nernst equation. The concentrations entered in the Species Matching section of the **Chemistry** interface will be used to calculate the equilibrium potential. The reference concentrations, defined in the Reference Concentrations section, will be used to compute the activities in the reaction quotient expression, Q_r.

Automatic
This option is only available if the **Calculate mixture properties** check box in the Calculate Transport Properties section is checked.

The Species enthalpies and entropies are used to calculate the equilibrium potential of the electrode reaction at the temperature and composition of the system.

If only species enthalpies and entropies at standard state are available, use the Nernst Equation option instead.

REFERENCE CONCENTRATIONS

The reference concentrations for the species in the reaction can be changed here.

Automatic

The phase indicated when first naming a species will be used to select a suitable reference concentration. The species must indicate the phase in the name when the species is first created.

For aqueous dilute species, denoted by (aq) in their names, the activity is calculated as their concentration divided by 1 M. For gaseous species, denoted by (g) in their names, the activity is calculated as their concentration divided by the standard reference pressure of 1 atm, converted into concentration using the ideal gas law. For solid species, denoted by (s) in their names, the reference concentration 1. For surface species, denoted by (ads) in their names, the reference surface concentration will be set to the site density configured in the Species Matching section. Any species not containing a phase in their name, will use a reference state depending on the phase selected under Mixture Properties. If the phase is Gas, the gaseous species reference concentration described above will be used, while if the phase is Liquid, the aqueous species 1 M reference concentration will be used.

User Defined

The reference concentrations for each type of species can be set manually, for aqueous, gaseous, solid, surface, and any other species, respectively.

ELECTRODE KINETICS

See the Electrode Reaction node in Shared Physics Features in the Current Distribution Interfaces for a general description of the Electrode Kinetics section.

Electrode reactions in the Chemistry interface support **User-defined**, **Butler-Volmer**, and **Linearized Butler-Volmer** kinetics. For the latter two options, **User-defined** exchange current densities and exchange current densities according to the **Mass Action Law** are supported.

If the equilibrium potential is calculated using **Nernst Equation**, the exponents in the local current density expression are evaluated using the reference overpotential. If

instead the equilibrium potential is calculated using the **Automatic** option, the exponents are evaluated using the overpotential.

HEAT OF REACTION

See the Electrode Reaction node in Shared Physics Features in the Current Distribution Interfaces for a general description of the Heat of Reaction section. Electrode Reactions in Chemistry do not support the **Temperature Derivative** option.

By choosing **Automatic**, the **Thermoneutral voltage** parameter, E_{therm} (SI unit: V), will be calculated according to

$$E_{\text{therm}} = -\frac{\Delta_r H}{nF} \tag{5-16}$$

using the Species enthalpies.

⊙	• Electrode Reactions Theory
	• Electrode Kinetics Expressions

Electrode Reaction Group

To add an **Electrode Reaction Group** node (🧪) either right-click the **Chemistry** node or in the **Chemistry** toolbar click **Electrode Reaction Group**.

An **Electrode Reaction Group** is typically used to represents all electrode reactions occurring on one electrode.

Multiple Electrode Reaction nodes may be added to the **Electrode Reaction Group**. Variables for the sum of all electrode reactions in one group can be used as input in **Electrode Reaction** features in current distribution interfaces.

This node is available with a Battery Design Module, Corrosion Module, Electrochemistry Module, Electrodeposition Module, or Fuel Cell & Electrolyzer Module license.

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.

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, 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** (≡x) 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.

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.

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, 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 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.

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 automatically added when either the Reversible Reaction Group or the Equilibrium Reaction Group is used.

For the case of temperature dependent reaction kinetics, a Species Thermodynamics subnode is automatically created in which the thermodynamic properties of the species can be specified.

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, 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.

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 • Space Charge Density Coupling • Potential Coupling
▥	*Diffuse Double Layer*: Application Library path **Fuel_Cell_and_Electrolyzer_Module/General_Electrochemistry/** **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 autoionization 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.

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**. Use the conservative formulation 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 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 pK_a (the acid equilibrium constant) parameter. For the weak bases the pK_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 an 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 the 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 **Linderstrøm-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 pK_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**, $\phi_{l, \text{bnd}}$ (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 an 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 are the dominating transport mechanisms 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
②	• Theory for the Surface Reactions Interface

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: mol/m^2). The default is 2×10^{-5} 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·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, $R_{b,cb1,cb2...}$ (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, $c_{s,0,cs1,cs2...}$ (SI unit: $\text{mol}/(\text{m}^2 \cdot \text{s})$).

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 Interfaces

The Fuel Cell & Electrolyzer Module includes predefined multiphysics interfaces that couple fluid with mass transport and reactions.

Selecting any of these interfaces under the **Chemical Species Transport>Reacting Flow** or **Chemical Species Transport>Reacting Flow in Porous Media** branches of the **Model Wizard** or **Add Physics** windows, adds a fluid flow interface and either a **Transport of Diluted Species** or **Transport of Concentrated Species** interface to the Model Builder.

In addition, the Multiphysics node **Reacting Flow** is added. The **Reacting Flow** node predefines and controls the couplings between the mass and fluid transport 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 **Porous Medium** 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. When a **Heat Transfer** and a **Chemistry** interface are selected, use this coupling to simulate heat transfer additionally to mass transport and reactions.

The coupling adds the heat source of reaction when a heat transfer interface is selected. No additional heat source needs to be defined to account for it in the heat transfer interface. It also accounts for the multiphysics stabilization terms, for work due to pressure forces and viscous dissipation.

Select a **Fluid Flow** interface and a **Species transport** interface to couple fluid flow with mass transport. **Chemistry** and **Heat Transfer** are optional. They can be set to **None** when the coupling is used to simulate isothermal mixtures.

When a **Chemistry** interface is selected and **Heat Transfer** is set to **None**, fluid properties are taken from the Chemistry interface. Set the **Temperature** to evaluate the fluid properties synchronized with all the physics interfaces at the given temperature.

Select a **Chemistry** interface and **Heat Transfer** interface in order to account for the heat of reaction, enthalpy diffusion, viscous heating and mass fluxes contributing to the heat and energy balance.

📝   When **Chemistry** is set to **None** and a **Heat Transfer** interface is selected, the coupling is solved in the same way as when no Heat Transfer interface is selected. Thermodynamic properties are required by the Heat Transfer interface.

The pressure, velocity, and temperature variables of the **Reacting Flow** coupling node are set to the **Common Model Input** values of the **Default Model Inputs** node on the complementary selection, that is, all domains except those from the **Selection** list. It allows to couple multiple fluid flow or transport of species interfaces with a single heat transfer interface. See Default Model Inputs in the *COMSOL Multiphysics Reference Manual* for details.

DOMAIN LEVEL SYNCHRONIZATION

The **Reacting Flow** coupling synchronizes the features from a Chemistry interface, Heat Transfer interface, Single-Phase Flow, or Brinkman Equations, interface and a Transport of Concentrated Species interface. When the Chemistry interface is not selected, the density in the Single-Phase Flow interface is automatically synchronized to the one defined by the Transport of Concentrated Species interface.

The velocity field used by the Transport of Concentrated Species interface and Heat Transfer interface is synchronized to the one computed in the Single-Phase Flow interface.

When a Chemistry interface is selected, the **Reacting Flow** coupling synchronizes the definition of the thermal conductivity, density, heat capacity, enthalpy, and dynamic viscosity with the other coupled physics interfaces. The reference temperature is taken from the Heat Transfer 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.

TURBULENT MASS TRANSFER

When a turbulence model is used, the **Reacting Flow** coupling applies turbulence modeling for the mass transport in the following manners:

- Turbulent heat transfer and mass transport are added, defined from the turbulent viscosity and a turbulent Schmidt number (for more information, see Turbulent Mass Transport Models).

- Temperature and mass transport wall functions. When a turbulence model using wall functions is used for the fluid flow, the Reacting Flow coupling automatically adds wall functions for the temperature and mass transport on the same boundaries (for more information, see Mass Transport Wall Functions).

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 `nirf1`.

DOMAIN SELECTION

The **Reacting Flow** coupling is automatically defined on the intersection of the selections for the coupled interfaces. When modeling porous media transport a **Porous Medium** feature, applied on the same domains, is needed in all coupled transport interfaces. **Reacting Flow** coupling supports porous media transport in **Fluid flow** and **Species transport** 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, Species transport, Chemistry, Heat Transfer** 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 a list to uncouple the node from a physics interface.

Click the **Go to Source** buttons (![icon]) to move to the main physics interface node for the selected physics interface.

Click the **Show or Hide Physics Properties Settings** button (![icon]) to toggle the display of physics properties settings affecting the coupling feature. When a turbulence model is used, turbulent heat and mass transfer is automatically accounted for (see the settings in the **Turbulence** section below). Using Reacting Flow, the heat and 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*.

> ![note icon] 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, Species transport, Chemistry** and **Heat Transfer** 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*.

MASS TRANSPORT TURBULENCE MODEL

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.

HEAT TRANSFER TURBULENCE MODEL

This section is available when a Heat Transfer interface is selected and the fluid flow interface uses a turbulence model. Select an option from the **Heat transport turbulence model** list: **Kays-Crawford** (the default), **Extended Kays-Crawford**, or **User-defined turbulent Prandtl number**.

For **Extended Kays-Crawford**, enter a **Reynolds number at infinity** $\mathrm{Re}_{\mathrm{inf}}$ (dimensionless).

For **User-defined turbulent Prandtl number**, enter a **Turbulent Prandtl number** pr_T (dimensionless).

When the flow interface uses a RANS turbulence model, the conductive heat flux is defined as

$$q = -(k + k_\mathrm{T})\nabla T$$

with the turbulent thermal conductivity defined as

$$k_\mathrm{T} = \frac{\mu_\mathrm{T} C_p}{\mathrm{Pr}_\mathrm{T}}$$

where μ_T is defined by the flow interface, and Pr_T depends on the **Heat transport turbulence model**. See Turbulent Conductivity for details.

The **Turbulence model type** used by the fluid flow interface can be displayed by selecting the **Show or Hide Physics Property Settings** button at the right of the **Fluid flow** list.

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 Interfaces

The Fuel Cell & Electrolyzer 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. A **Porous Material** node, including a **Fluid** and a **Solid** subnode, is also added to the component.

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 **Porous Medium** 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 solutes, dissolved in a solvent of significantly higher concentration. A **Porous Medium** feature is active by default on the entire interface selection.

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. A **Porous Material** node is also added to the component.

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 **Porous Medium** feature is active by default on the entire interface selection.

The **Transport of Concentrated Species in Porous Media** interface solves for an arbitrary number of mass fractions in free and porous media. In the current multiphysics interface a **Porous Medium** 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 *Chemical Reaction Engineering Module User's Guide*.

The Reacting Flow Coupling Feature

For the settings of this feature see The Reacting Flow Coupling Feature in the *Chemical Reaction Engineering Module User's Guide*.

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 section.

TRANSPORT OF CONCENTRATED SPECIES

The available physics features for The Transport of Concentrated Species interface are listed in the section.

The Nonisothermal Reacting Flow Multiphysics Interfaces

Nonisothermal Reacting Flow is a predefined multiphysics interface, available in the Fuel Cell & Electrolyzer Module, that couples fluid flow and heat transfer with species transport and reactions.

Selecting an entry in the **Chemical Species Transport>Nonisothermal Reacting Flow** branch of the **Model Wizard**, or **Add Physics** windows, the following four physics interfaces are added to the Model Builder:

- **Chemistry**
- **Transport of Concentrated Species**
- **Laminar Flow**, or a turbulent flow equivalent like **Turbulent Flow, k-ε**.
- **Heat Transfer in Fluids**

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 set up of models.

In this section:

- The Nonisothermal Reacting Laminar Flow Interface
- The Nonisothermal Reacting Turbulent Flow, k-e Interface
- The Nonisothermal Reacting Turbulent Flow, k-w Interface
- The Nonisothermal Reacting Turbulent Flow, SST Interface
- The Nonisothermal Reacting Turbulent Flow, Low Re k-e Interface
- The Reacting Flow Coupling Feature
- Physics Interface Features

The Nonisothermal Reacting Laminar Flow Interface

The **Nonisothermal Reacting Laminar Flow** ( ) multiphysics interface is used to simulate laminar flow and heat transfer coupled to species transport in a gas or liquid moving either in a free flow or through the interstices of a porous medium.

It combines the **Chemistry**, **Transport of Concentrated Species**, **Laminar Flow**, and **Heat Transfer in Fluids** interfaces. The **Reacting Flow** multiphysics coupling, which is added automatically, couples fluid flow, heat transfer, and mass transfer. The species transport supports both a mixture, where the concentrations are of comparable order of magnitude, and low-concentration solutes in a solvent.

The multiphysics coupling takes into account the heat of reaction in the fluid and at the surface of a porous catalyst, enthalpy diffusion, and contributing mass fluxes. In addition, the temperature dependency of the chemical properties and reactions are accounted for.

The interface can be used for stationary and time-dependent analysis in 2D, 2D axial symmetry, and 3D.

On the constituent physics interfaces:

The **Chemistry** interface defines thermodynamic properties and transport properties of the fluid. Provided that properties of each species have been defined, composition dependent mixture properties such as the heat capacity, the density, and the heat conduction are defined. The **Chemistry** interface also defines reaction rates for species involved in the chemical reactions added to the system.

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. A **Transport Properties** feature is active by default on the entire interface selection

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.

The **Heat Transfer** interface solves for conservation of energy. A **Fluid** feature is active by default on the entire interface selection.

The Nonisothermal Reacting Turbulent Flow, k-ε Interface

The **Nonisothermal Reacting Turbulent Flow, k-ε** ( ) multiphysics interface is used to simulate flow in the turbulent regime, heat transfer, and species transport and in a gas or liquid moving either in a free flow or through the interstices of a porous medium. This interface requires a license for either the CFD Module or the Heat Transfer Module.

It combines the **Chemistry**, **Transport of Concentrated Species**, **Turbulent Flow, k-ε**, and **Heat Transfer in Fluids** interfaces. The **Reacting Flow** multiphysics coupling, which is added automatically, couples fluid flow, heat transfer and mass transfer. The species transport supports both a mixture, where the concentrations are of comparable order of magnitude, and low-concentration solutes in a solvent.

The multiphysics coupling takes into account the heat of reaction in the fluid and at the surface of a porous catalyst, enthalpy diffusion, and contributing mass fluxes. In addition, the temperature dependency of the chemical properties and reactions are accounted for.

The interface can be used for stationary and time-dependent analysis in 2D, 2D axial symmetry, and 3D.

On the constituent physics interfaces:

The **Chemistry** interface defines thermodynamic properties and transport properties of the fluid. Provided that properties of each species have been defined, composition dependent mixture properties such as the heat capacity, the density, and the heat conduction are defined. The **Chemistry** interface also defines reaction rates for species involved in the chemical reactions added to the system.

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. Mass transfer close to walls is modeled using wall functions

The equations solved by the **Turbulent Flow, k**-ε interface are the Navier–Stokes equations for conservation of momentum and the continuity equation for conservation of mass. Turbulence effects are modeled using the standard two-equation k-ε model with realizability constraints. Flow close to walls is modeled using wall functions.

The **Heat Transfer** interface solves for conservation of energy. A **Fluid** feature is active by default on the entire interface selection. Heat transfer close to walls is modeled using wall functions.

The Nonisothermal Reacting Turbulent Flow, k-ω Interface

The **Nonisothermal Reacting Turbulent Flow, k-**ω (〰) multiphysics interface is used to simulate flow in the turbulent regime, heat transfer, and species transport and in a gas

or liquid moving either in a free flow or through the interstices of a porous medium. This interface requires a license for the CFD Module.

It combines the **Chemistry**, **Transport of Concentrated Species**, **Turbulent Flow, k-**ω, and **Heat Transfer in Fluids** interfaces. The **Reacting Flow** multiphysics coupling, which is added automatically, couples fluid flow, heat transfer and mass transfer. The species transport supports both a mixture, where the concentrations are of comparable order of magnitude, and low-concentration solutes in a solvent.

The multiphysics coupling takes into account the heat of reaction in the fluid and at the surface of a porous catalyst, enthalpy diffusion, and contributing mass fluxes. In addition, the temperature dependency of the chemical properties and reactions are accounted for.

The interface can be used for stationary and time-dependent analysis in 2D, 2D axial symmetry, and 3D.

On the constituent physics interfaces:

The **Chemistry** interface defines thermodynamic properties and transport properties of the fluid. Provided that properties of each species have been defined, composition dependent mixture properties such as the heat capacity, the density, and the heat conduction are defined. The **Chemistry** interface also defines reaction rates for species involved in the chemical reactions added to the system.

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. Mass transfer close to walls is modeled using wall functions

The equations solved by the **Turbulent Flow, k**-ω interface are the Navier–Stokes equations for conservation of momentum and the continuity equation for conservation of mass. The fluid flow turbulence is modeled using the Wilcox revised k-ω model with realizability constraints. Flow close to walls is modeled using wall functions.

The **Heat Transfer** interface solves for conservation of energy. A **Fluid** feature is active by default on the entire interface selection. Heat transfer close to walls is modeled using wall functions.

The Nonisothermal Reacting Turbulent Flow, SST Interface

The **Nonisothermal Reacting Turbulent Flow, SST** ( ) multiphysics interface is used to simulate flow in the turbulent regime, heat transfer, and species transport and in a gas or liquid moving either in a free flow or through the interstices of a porous medium. This interface requires a license for either the CFD Module or the Heat Transfer Module.

It combines the **Chemistry**, **Transport of Concentrated Species**, **Turbulent Flow, SST**, and **Heat Transfer in Fluids** interfaces. The **Reacting Flow** multiphysics coupling, which is added automatically, couples fluid flow, heat transfer and mass transfer. The species transport supports both a mixture, where the concentrations are of comparable order of magnitude, and low-concentration solutes in a solvent.

The multiphysics coupling takes into account the heat of reaction in the fluid and at the surface of a porous catalyst, enthalpy diffusion, and contributing mass fluxes. In addition, the temperature dependency of the chemical properties and reactions are accounted for.

The interface can be used for stationary and time-dependent analysis in 2D, 2D axial symmetry, and 3D.

On the constituent physics interfaces:

The **Chemistry** interface defines thermodynamic properties and transport properties of the fluid. Provided that properties of each species have been defined, composition dependent mixture properties such as the heat capacity, the density, and the heat conduction are defined. The **Chemistry** interface also defines reaction rates for species involved in the chemical reactions added to the system.

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. Mass transfer close to walls is modeled using wall functions

The equations solved by the **Turbulent Flow, SST** interface are the Navier–Stokes equations for conservation of momentum and the continuity equation for conservation of mass. The fluid flow turbulence is modeled using the SST model. The SST model is a low-Reynolds number model which means that it resolves the velocity, pressure, and concentrations all the way down to the wall. For that reason this physics interface is suited for studying mass transfer at high Schmidt numbers. The SST model

depends on the distance to the closest wall, and the interface therefore includes a wall distance equation.

The **Heat Transfer** interface solves for conservation of energy. A **Fluid** feature is active by default on the entire interface selection. Heat transfer close to walls is modeled using wall functions.

The Nonisothermal Reacting Turbulent Flow, Low Re k-ε Interface

The **Nonisothermal Reacting Turbulent Flow, Low Re k-ε** ( ) multiphysics interface is used to simulate flow in the turbulent regime, heat transfer, and species transport and in a gas or liquid moving either in a free flow or through the interstices of a porous medium. This interface requires a license for either the CFD Module or the Heat Transfer Module.

It combines the **Chemistry**, **Transport of Concentrated Species**, **Turbulent Flow, Low Re k-ε**, and **Heat Transfer in Fluids** interfaces. The **Reacting Flow** multiphysics coupling, which is added automatically, couples fluid flow, heat transfer and mass transfer. The species transport supports both a mixture, where the concentrations are of comparable order of magnitude, and low-concentration solutes in a solvent.

The multiphysics coupling takes into account the heat of reaction in the fluid and at the surface of a porous catalyst, enthalpy diffusion, and contributing mass fluxes. In addition, the temperature dependency of the chemical properties and reactions are accounted for.

The interface can be used for stationary and time-dependent analysis in 2D, 2D axial symmetry, and 3D.

On the constituent physics interfaces:

The **Chemistry** interface defines thermodynamic properties and transport properties of the fluid. Provided that properties of each species have been defined, composition dependent mixture properties such as the heat capacity, the density, and the heat conduction are defined. The **Chemistry** interface also defines reaction rates for species involved in the chemical reactions added to the system.

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. Mass transfer close to walls is modeled using wall functions

The equations solved by the **Turbulent Flow, Low Re k-ε** interface are the Navier–Stokes equations for conservation of momentum and the continuity equation for conservation of mass. The fluid flow turbulence is modeled using the AKN low-Reynolds number k-e model. The low-Reynolds number model resolves the velocity, pressure, and concentrations all the way down to the wall. For that reason this physics interface is suited for studying mass transfer at high Schmidt numbers. The AKN model depends on the distance to the closest wall, and the interface therefore includes a wall distance equation.

The **Heat Transfer** interface solves for conservation of energy. A **Fluid** feature is active by default on the entire interface selection. Heat transfer close to walls is modeled using wall functions.

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).

> 🔆 In general, to add a node, go to the **Physics** toolbar, no matter what operating system you are using.

CHEMISTRY

The available physics features for the Chemistry interface are listed in the section Feature Nodes Available for the Chemistry Interface.

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 *CFD Module User's Guide*.

TURBULENT FLOW

The available physics features for a single-phase flow interface using a turbulence model, for example the Turbulent Flow, k-ε interface, is listed in the section Domain,

Boundary, Pair, and Point Nodes for Single-Phase Flow in the *CFD Module User's Guide*.

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.

HEAT TRANSFER

The available physics features for the Heat Transfer interface are listed in the section The Heat Transfer Features in the *COMSOL Multiphysics Reference Manual*.

Theory for the Transport of Diluted Species Interface

 provides a predefined modeling environment for studying the evolution of chemical species transported by diffusion and convection. The physics interface assumes that all species present are dilute; that is, that their concentration is low 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
- 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 :

- 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:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{J}_i + \mathbf{u} \cdot \nabla c_i = R_i \tag{5-17}$$

Equation 5-17 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

$$\mathbf{J}_i = -D\nabla c_i \tag{5-18}$$

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 5-17 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 5-17), 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:

$$K_{eq} = \frac{\displaystyle\prod_{i \in \text{products}} a_i^{\nu_i}}{\displaystyle\prod_{i \in \text{reactants}} a_i^{-\nu_i}}$$

where the species activities are defined as

$$a_i = \gamma_{c,i}\frac{c_i}{c_{a0}}$$

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 in 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 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 5-17.

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:

$$\text{nonconservative: } \frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c = \nabla \cdot \mathbf{J}_i + R \tag{5-19}$$

$$\text{conservative: } \frac{\partial c}{\partial t} + \nabla \cdot (c\mathbf{u}) = \nabla \cdot \mathbf{J}_i + R \tag{5-20}$$

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 5-19 and Equation 5-20 by clearing the Convection check box in the Transport Mechanisms section for . 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, 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

$$\lim_{\delta V \to 0} \int_{\delta V} Q_c = \dot{q}_{p,c} \tag{5-21}$$

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 5-21, 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 5-21 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 $Q_{l,c}$ (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

$$\lim_{\delta S \to 0} \int_{\delta S} Q_{l,c} = q_{l,c} \tag{5-22}$$

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

$$q_{l,c}\text{test}(c)$$

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.

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:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i - z_i u_{m,i} F c_i \nabla V + c_i \mathbf{u}) \ = \ R_i \qquad (5\text{-}23)$$

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
- $u_{m,i}$ (SI unit: mol·s/kg) is its ionic mobility

In this case the diffusive flux vector is

$$\mathbf{J}_i \ = \ -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla V$$

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 electroactive 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:

$$\mathbf{i} = F\sum_j -z_j^2 u_{m,j} F c_j \nabla \phi \tag{5-24}$$

Equation 5-24 is simply Ohm's law for ionic current transport and can be simplified to

$$\mathbf{i} = -\kappa \nabla \phi \tag{5-25}$$

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 5-25, yields:

$$\nabla \cdot (-\kappa \nabla \phi) = 0 \tag{5-26}$$

Equation 5-26 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 Péclet 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 Péclet 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

$$\mathbf{n} \cdot (\mathbf{J}_i + \mathbf{u}c_i) = \mathbf{n} \cdot (\mathbf{u}c_{i,\,0}) \tag{5-27}$$

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:

$$\frac{\partial}{\partial t}(\theta_l c_i) + \frac{\partial}{\partial t}(\rho c_{P,i}) + \frac{\partial}{\partial t}(\theta_g c_{G,i}) + \mathbf{u} \cdot \nabla c_i =$$
$$\nabla \cdot [(D_{D,i} + D_{e,i})\nabla c_i] + R_i + S_i$$

(5-28)

On the left-hand side of Equation 5-28, 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 5-28 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 5-28, 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 5-28 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, $c_{P,i}$, 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

$$\frac{\partial}{\partial t}(\rho c_{P,i}) = \rho \frac{\partial c_{P,i}}{\partial c_i} \frac{\partial c_i}{\partial t} - c_{P,i} \rho_s \frac{\partial \varepsilon_P}{\partial t} = \rho K_{P,i} \frac{\partial c_i}{\partial t} - c_{P,i} \rho_s \frac{\partial \varepsilon_P}{\partial t} \tag{5-29}$$

where $K_{P,i} = \partial c_{P,i}/\partial c_i$ 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, $c_{G,i}$, is a linear function of the liquid phase concentration, the volatilization term is defined as

$$\frac{\partial}{\partial t}\theta_g c_{G,i} = \theta_g \frac{\partial c_{G,i}}{\partial c_i} \frac{\partial c_i}{\partial t} + k_{G,i} c_i \frac{\partial \theta_g}{\partial t} = \theta_g k_{G,i} \frac{\partial c_i}{\partial t} + k_{G,i} c_i \frac{\partial \theta_g}{\partial t} \tag{5-30}$$

where $k_{G,i} = \partial c_{G,i}/\partial c_i$ 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

$$\frac{\partial}{\partial t}(\varepsilon_p c_i) + \frac{\partial}{\partial t}(\rho c_{P,i}) + \mathbf{u} \cdot \nabla c_i = \nabla \cdot [(D_{D,i} + D_{e,i})\nabla c_i] + R_i + S_i \tag{5-31}$$

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 $\mathbf{u}$ 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.
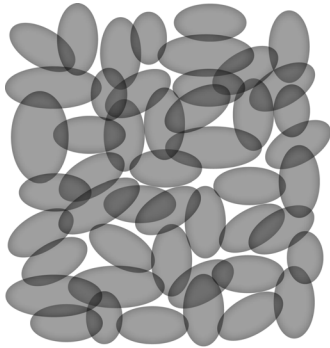
Figure 5-4: A block of a porous medium consisting of solids and the pore space between the solid grains. The average linear velocity describes how fast the fluid moves within the pores. The Darcy velocity attributes this flow over the entire fluid-solid face.

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 5-28 is written as:

$$\frac{\partial}{\partial t}(\theta_l c_i) + \frac{\partial}{\partial t}(\rho c_{P,i}) + \frac{\partial}{\partial t}(\theta_g c_{G,i}) + \nabla \cdot \mathbf{u} c_i =$$
$$\nabla \cdot [(D_{D,i} + D_{e,i})\nabla c_i] + R_i + S_i \tag{5-32}$$

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 5-28.

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 or in saturated or unsaturated porous media, the effective diffusivity is defined as:

$$D_e = D_F \qquad \text{Free Flow}$$

$$D_e = \frac{\varepsilon_p}{\tau_L} D_L \qquad \text{Saturated Porous Media}$$

$$D_e = \frac{\theta_l}{\tau_L} D_L \qquad \text{Unsaturated Porous Media}$$

$$D_e = \frac{\theta_l}{\tau_L} D_L + \frac{\theta_g}{\tau_G} k_G D_G \quad \text{Unsaturated with Volatilization}$$

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. 3):

$$\tau_L = \theta_l^{-7/3}\varepsilon_p^{\ 2}, \tau_G = \theta_g^{-7/3}\varepsilon_p^{\ 2}$$

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 low.

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 rate is low relative to the mechanical dispersion, except at very low fluid velocities.
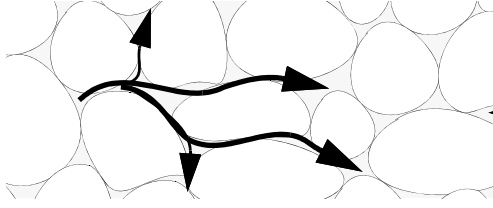
Figure 5-5: Spreading of fluid around solid particles in a porous medium.

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. 5):

$$D_{Dii} = \alpha_L \frac{u_i^2}{|\mathbf{u}|} + \alpha_T \frac{u_j^2}{|\mathbf{u}|}$$

$$D_{Dij} = D_{Dji} = (\alpha_L - \alpha_T) \frac{u_i u_j}{|\mathbf{u}|}$$

In these equations, D_{Dii} (SI unit: m^2/s) are the principal components of the dispersivity tensor, and D_{Dji} and D_{Dji} 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. 4) can be used. Consider a transverse isotropic media, where the strata are piled up in the z direction, the dispersivity tensor components are:

$$D_{\mathrm{L}xx} = \alpha_1 \frac{u^2}{|\mathbf{u}|} + \alpha_2 \frac{v^2}{|\mathbf{u}|} + \alpha_3 \frac{w^2}{|\mathbf{u}|}$$

$$D_{\mathrm{L}yy} = \alpha_1 \frac{v^2}{|\mathbf{u}|} + \alpha_2 \frac{u^2}{|\mathbf{u}|} + \alpha_3 \frac{w^2}{|\mathbf{u}|}$$

$$D_{\mathrm{L}zz} = \alpha_1 \frac{w^2}{|\mathbf{u}|} + \alpha_3 \frac{u^2}{|\mathbf{u}|} + \alpha_3 \frac{v^2}{|\mathbf{u}|} \qquad (5\text{-}33)$$

$$D_{\mathrm{L}xy} = D_{\mathrm{L}yx} = (\alpha_1 - \alpha_2)\frac{uv}{|\mathbf{u}|}$$

$$D_{\mathrm{L}xz} = D_{\mathrm{L}zx} = (\alpha_1 - \alpha_3)\frac{uw}{|\mathbf{u}|}$$

$$D_{\mathrm{L}yz} = D_{\mathrm{L}zy} = (\alpha_1 - \alpha_3)\frac{vw}{|\mathbf{u}|}$$

In Equation 5-33 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. 5 and Ref. 6).

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. 7). 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:

$$c_P = c_{Pmax}\frac{K_L c}{1 + K_L c} \qquad\qquad \text{Langmuir}$$

$$c_P = K_F\left(\frac{c}{c_{ref}}\right)^N \qquad\qquad \text{Freundlich}$$

$$c_P = c_{Pmax}\frac{b_T c}{(1 + (b_T c)^{N_T})^{1/N_T}} \qquad\qquad \text{Toth} \qquad\qquad (5\text{-}34)$$

$$c_P = \frac{K_B c_0 c}{(c_S - c)\left(1 + (K_B - 1)\frac{c}{c_S}\right)} \qquad\qquad \text{BET}$$

The above equations contains the following parameters:

- Freundlich (Ref. 8)
  - Freundlich constant K_F (SI unit:·mol/kg), Freundlich exponent N_F (dimensionless), and reference concentration c_{ref} (SI unit: mol/m^3).
- Langmuir (Ref. 9)
  - Langmuir constant K_L (SI unit: m^3/mol), and adsorption maximum c_{Pmax} (SI unit: mol/kg).
- Toth (Ref. 10)
  - Toth constant b_T (SI unit: m^3/mol), Toth exponent N_T (dimensionless), and adsorption maximum c_{Pmax} (SI unit: mol/kg).
- BET (Brunauer–Emmett–Teller, Ref. 11)
  - BET constant K_B (dimensionless), the monolayer adsorption capacity c_0 (SI unit: mol/kg) and the 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. Applying the isotherms, as defined in the Adsorption section above, assumes that adsorption is at equilibrium locally. This implies that the species phase transfer, between the fluid and the solid phase (within the porous medium), is much faster than the transport within the fluid phase.

Using a Species Source feature, arbitrary expressions can be entered to define, for example, nonequilibrium and temperature-dependent adsorption laws, in the manner of Fetter (Ref. 12), or Bear and Verruijt (Ref. 13).

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 lower 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:

$$R_{Li} = -\theta\frac{\ln 2}{\lambda_{Li}}c_i \qquad \text{Radioactive decay — liquid}$$

$$R_{Pi} = -\rho_b\frac{\ln 2}{\lambda_{Pi}}\Big(\frac{\partial c_{Pi}}{\partial c_i}\Big)c_i \quad \text{Radioactive decay — solid}$$

$$R_{Gi} = -\frac{\ln 2}{\lambda_{Gi}}a_v\Big(\frac{\partial c_{Gi}}{\partial c}\Big)c_i \quad \text{Radioactive decay — gas}$$

$$R_{Lk} = \theta\zeta_{Li}c_i \qquad \text{Creation from parent } c_{Li} \text{ — liquid}$$

$$R_{Pk} = \rho_b\zeta_{Pi}\Big(\frac{\partial c_{Pi}}{\partial c_i}\Big)c_i \quad \text{Creation from sorbed parent } c_{Pi} \text{ — solid}$$

$$R_{Gk} = -\zeta a_v\Big(\frac{\partial c_{Gi}}{\partial c}\Big)c_i \quad \text{Reaction — gas}$$

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. 14:

$$\zeta_T = \zeta_R \exp\left[\frac{E_a(T - T_R)}{R_u T T_R}\right] \tag{5-35}$$

In Equation 5-35, 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 5-28. The resulting equation is:

$$d_{fr}\left(\frac{\partial \rho_b c_{P,i}}{\partial t} + \frac{\partial \varepsilon_p c_i}{\partial t} + \nabla_t \cdot (D_{e,i}\nabla_t c_i) + \mathbf{u}\cdot\nabla_t c_i\right) = d_{fr}R_i + d_{fr}S_i + n_0 \tag{5-36}$$

Here d_{fr} is the fracture thickness, $c_{P,i}$ 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 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 5-36. See for more information about the physics interface solving the equation on boundaries only.

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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
- 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 5-37 then describes the mass transport for an individual species:

$$\frac{\partial}{\partial t}(\rho \omega_i) + \nabla \cdot (\rho \omega_i \mathbf{u}) = -\nabla \cdot \mathbf{j}_i + R_i \qquad (5\text{-}37)$$

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 5-38 for the conservation of mass

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \qquad (5\text{-}38)$$

assuming that

$$\sum_{i=1}^{Q} \omega_i = 1, \ \sum_{i=1}^{Q} \mathbf{j}_i = 0, \ \sum_{i=1}^{Q} R_i = 0$$

Using the mass conservation equation, the species transport for an individual species, i, is given by:

$$\rho \frac{\partial}{\partial t}(\omega_i) + \rho (\mathbf{u} \cdot \nabla) \omega_i = -\nabla \cdot \mathbf{j}_i + R_i \qquad (5\text{-}39)$$

$Q - 1$ of the species equations are independent and possible to solve for using Equation 5-39. 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:

$$\omega_1 = 1 - \sum_{i=2}^{Q} \omega_i \qquad (5\text{-}40)$$

Multicomponent Gas Diffusion: Maxwell–Stefan Description

The Maxwell–Stefan formulation for a multicomponent mixture defines $N - 1$ (with N being the number of active species in the model) force balances according to

$$-\sum_{k \neq i} \frac{x_i x_k}{D_{ik}} \left(\frac{\mathbf{j}_i}{\omega_i \rho} - \frac{\mathbf{j}_k}{\omega_k \rho} \right) = \mathbf{d}_k - \sum_{k \neq i} \frac{x_i x_k}{D_{ik}} \left(\frac{D_k^{\mathrm{T}}}{\omega_k \rho} - \frac{D_i^{\mathrm{T}}}{\omega_i \rho} \right) \nabla \ln T \qquad (5\text{-}41)$$

where

- D_{ik} (SI unit: m^2/s) are the binary Maxwell–Stefan 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.

By inverting the above set of equations, the mass flux relative to the mass average velocity, $\mathbf{j}_i$, can be defined by the generalized Fick equations (Ref. 1):

$$\mathbf{j}_i = -\rho\omega_i \sum_{k=1}^{Q} \tilde{D}_{ik}\mathbf{d}_k - D_i^T \nabla \ln T \tag{5-42}$$

where $\tilde{D}_{ik}$ (SI unit: m^2/s) are the multicomponent Fick diffusivities.

For ideal gas mixtures the diffusional driving force is (Ref. 1)

$$\mathbf{d}_k = \frac{1}{cR_gT}\left[\nabla p_k - \omega_k\nabla p - \rho_k\mathbf{g}_k + \omega_k \sum_{l=1}^{Q} \rho_l\mathbf{g}_l\right] \tag{5-43}$$

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 5-42 and Equation 5-43, 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

$$\mathbf{d}_k = \nabla x_k + \frac{1}{p}\left[(x_k - \omega_k)\nabla p - \rho\omega_k\mathbf{g}_k + \omega_k \sum_{l=1}^{Q} \rho\omega_l\mathbf{g}_l\right] \tag{5-44}$$

The mole fraction x_k is given by

$$x_k = \frac{\omega_k}{M_k}M \tag{5-45}$$

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

$$\rho \frac{\partial}{\partial t}(\omega_i) + \rho(\mathbf{u} \cdot \nabla)\omega_i = \nabla \cdot \left(\rho\omega_i \sum_{k=1}^{Q} \tilde{D}_{ik}\mathbf{d}_k + D_i^T \frac{\nabla T}{T} \right) + R_i$$

$$\mathbf{d}_k = \nabla x_k + \frac{1}{p}\left[(x_k - \omega_k)\nabla p - \rho\omega_k\mathbf{g}_k + \omega_k \sum_{l=1}^{Q} \rho\omega_l\mathbf{g}_l \right]$$

(5-46)

Multicomponent Diffusivities

The multicomponent Fick diffusivities, $\tilde{D}_{ik}$, are needed to solve Equation 5-46. 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)

$$\frac{x_i x_k}{D_{ik}} = -\omega_i \omega_k \frac{\sum_{j \neq i} (\mathrm{adj}B_i)_{jk}}{\sum_{j \neq i} \tilde{D}_{ij}(\mathrm{adj}B_i)_{jk}}, \quad (B_i)_{kj} = \tilde{D}_{kj} - \tilde{D}_{ij}, \qquad i \neq j$$

(5-47)

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 5-47 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:

$$\tilde{D}_{12} = \cfrac{-\cfrac{\omega_1(\omega_2 + \omega_3)}{x_1 D_{23}} - \cfrac{\omega_2(\omega_1 + \omega_3)}{x_2 D_{13}} + \cfrac{\omega_3^2}{x_3 D_{12}}}{\cfrac{x_1}{D_{12}D_{13}} + \cfrac{x_2}{D_{12}D_{23}} + \cfrac{x_3}{D_{23}D_{13}}}$$

For four components or more, COMSOL 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:

$$\tilde{D}_{ij} = N_{ij} - q \qquad (5\text{-}48)$$

where ij, the indices in the matrices $\tilde{D}$ and N, range from 1 to the number of species, Q.

The elements of the matrix N in Equation 5-48 are defined as

$$N_{ij} = (P^{-1})_{ij} \qquad (5\text{-}49)$$

where P^{-1} is the inverse of a matrix P defined as

$$P_{ij} = \frac{\omega_i \omega_j}{q} - \tilde{C}_{ij}$$

The matrix $\tilde{C}$ in turn is defined as

$$\tilde{C}_{ij} = \begin{cases} \dfrac{x_i x_j}{D_{ij}} & i \neq j \\[2ex] -\displaystyle\sum_{k \neq j} \tilde{C}_{ik} & i = j \end{cases}$$

The term q in Equation 5-48 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:

$$q = \sum_{i=1}^{n-1} \left(\sum_{j=i+1}^{n} D_{ij} \right)$$

Because the multicomponent Fick diffusivity matrix is symmetric, it is sufficient to apply Equation 5-49 to the upper triangle elements of $\check{D}$. 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:

$$\mathbf{j}_{\mathrm{md},\,i} = -\rho_i D_i^m \frac{\nabla x_i}{x_i} \tag{5-50}$$

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 5-50 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 5-50 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):

$$D_i^m = \frac{1 - \omega_i}{\displaystyle\sum_{k \ne i}^N \frac{x_k}{D_{ik}}} \tag{5-51}$$

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:

$$\mathbf{j}_{\mathrm{md},\,i} = -\rho_i D_i^{m\star} \frac{\nabla \omega_i}{\omega_i} = -\rho D_i^{m\star} \nabla \omega_i \tag{5-52}$$

For this assumption, using Equation 5-52 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):

$$\frac{1}{D_i^{m*}} = \sum_{k \neq i}^{N} \frac{x_k}{D_{ik}} + \frac{x_i}{1 - \omega_i} \sum_{k \neq i}^{N} \frac{\omega_k}{D_{ik}} \tag{5-53}$$

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:

$$\sum_{i = 1}^{N} \mathbf{j}_{md, i} = \sum_{i = 1}^{N} \rho \omega_i (\mathbf{u}_{d, i} + \mathbf{u}_c) = 0 \tag{5-54}$$

Hence the correction velocity is:

$$\mathbf{u}_c = -\sum_{i = 1}^{N} \omega_i \mathbf{u}_{d, i} \tag{5-55}$$

Here $\mathbf{u}_{d, i}$ is the diffusion velocity resulting from the flux assumption in Equation 5-50 or Equation 5-52. Note that the correction velocity is a constant correction (same for all species), but varies in space.

Using the correction velocity together with Equation 5-50 (flux proportional to the mole fraction gradient), the resulting diffusive flux is

$$\mathbf{j}_{md, i} = -\rho D_i^m \nabla \omega_i - \rho \omega_i D_i^m \frac{\nabla M}{M} + \rho \omega_i \sum_{i = 1}^{N} \frac{M_i}{M} D_i^m \nabla x_i \tag{5-56}$$

If instead Equation 5-52 is used (flux proportional to the mass fraction gradient), the resulting diffusive flux is

$$\mathbf{j}_{\mathrm{md},\,i} = -\rho D_i^{m\,*} \nabla \omega_i + \rho \omega_i \sum_{i\,=\,1}^{N} D_i^{m\,*} \nabla \omega_i \qquad (5\text{-}57)$$

PORE WALL INTERACTIONS

In porous media, the diffusion models may be extended to account for species collisions with the pore walls.

For the **Fick's law** or the **Mixture-averaged** diffusion models, the diffusion coefficient D_i^M is corrected with the **Wall diffusion** coefficient D_i^W in the following way

$$D_i^{MW} = \left(\frac{1}{D_i^M} + \frac{1}{D_i^W} \right)^{-1}$$

For the **Maxwell-Stefan** diffusion model, the following term is added to the species force balance (Equation 5-41)

$$\ldots + \frac{x_i}{D_{i,\,\mathrm{eff}}^W} \left(\frac{\mathbf{j}_i}{\omega_i \rho} + \mathbf{u}_W \right) = \mathbf{d}_i + \ldots$$

The wall velocity $\mathbf{u}_W$, representing the velocity of the fluid in a representative region adjacent to the pore wall, is here defined as

$$\mathbf{u}_W = -\frac{\dfrac{\nabla p_A}{p_A} + \sum_k \dfrac{x_k}{D_{k,\,\mathrm{eff}}^W} \dfrac{\mathbf{j}_k{'}}{\omega_k \rho}}{\sum_k \dfrac{x_k}{D_{k,\,\mathrm{eff}}^W}} \qquad (5\text{-}58)$$

where the modified fluxes $\mathbf{j}_k{'}$ have been calculated using the modified driving forces

$$\mathbf{d}_k{'} = \nabla x_k + \frac{1}{p} x_k \nabla p \qquad (5\text{-}59)$$

It should be noted that $\mathbf{u}_W$ can become nonzero also in the absence of pressure gradients. For a proper description of the fluid momentum balance, $\mathbf{u}_W$ needs to be added either as a contributing velocity (Darcy's law) or as a corresponding volume force $\mathbf{F} = \mu \kappa^{-1} \mathbf{u}_W$ (Brinkman equations).

The Maxwell–Stefan model formulated in this way correctly captures the Klinkenberg effect, and has large similarities with other models in literature incorporating Knudsen

diffusion such as the Dusty Gas Model and the (Modified) Binary Friction Model. In addition, for the limit of vanishing permeabilities ($\kappa \rightarrow 0$), the formulation reduces to the Lightfoot model for membrane transport.

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 ith 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

$$\mathbf{j}_{\text{md}, i} = -\rho_i D_{i, kl}^F \frac{\nabla x_i}{x_i} \tag{5-60}$$

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

$$\mathbf{j}_{\text{md}, i} = -\rho D_{i, kl}^F \nabla \omega_i \tag{5-61}$$

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

$$\mathbf{j}_{\mathrm{md},\,i} \;=\; -\rho D^{F}_{i,\,kl}\nabla\omega_{i} - \rho\omega_{i}D^{F}_{i,\,kl}\frac{\nabla M}{M} + \rho\omega_{i}\sum_{i\,=\,1}^{N}\frac{M_{i}}{M}D^{F}_{i,\,kl}\nabla x_{i} \qquad (5\text{-}62)$$

when using Equation 5-60 and

$$\mathbf{j}_{\mathrm{md},\,i} \;=\; -\rho D^{F}_{i,\,kl}\nabla\omega_{i} + \rho\omega_{i}\sum_{i\,=\,1}^{N}D^{F}_{i,\,kl}\nabla\omega_{i} \qquad (5\text{-}63)$$

when instead using Equation 5-61.

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^{T}_{i} . In a multicomponent mixture, the sum of the thermal diffusion coefficients is zero:

$$\sum_{i\,=\,1}^{Q} D^{T}_{i} \;=\; 0$$

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

$$R_i = \frac{1}{2} \frac{R_i^c - |R_i^c|}{\max(\omega_i, \omega_i^{dl})} \max(\omega_i, 0) + \frac{1}{2} \frac{R_i^c + |R_i^c|}{\max(1 - \omega_i, \omega_i^{dl})} \max(1 - \omega_i, 0) \qquad (5\text{-}64)$$

The first term on the right hand side of Equation 5-64 is active if $R_i^c < 0$, 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 $\omega_i > \omega_i^{dl}$. 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 5-64 is active if $R_i^c > 0$, 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 $\omega_i < 1 - \omega_i^{dl}$. 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

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Theory for 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

$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_l + \mathbf{u} c_i = \mathbf{J}_i + \mathbf{u} c_i \qquad (5\text{-}65)$$

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 .

CHARGE BALANCE EQUATION

The current vector, $\mathbf{i}_l$ (A/m^2), is defined as

$$\mathbf{i}_l = \sum_i z_i \mathbf{N}_i \qquad (5\text{-}66)$$

where the summation is made over all species in the electrolyte.

The governing equation for the electrolyte potential is

$$\nabla \cdot \mathbf{i}_l = Q_l \qquad (5\text{-}67)$$

where Q_l (SI unit: A/m^3) is the electrolyte current source stemming from, for example, porous electrode reactions. For nonporous 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

$$\sum_{i=1}^{N+2} z_i c_i = 0 \tag{5-68}$$

In water-based systems the species H+ and OH- are always present. The auto ionization reaction for water is

$$H_2O \leftrightarrow H^+ + OH^- \tag{5-69}$$

This reaction is fast, following the equilibrium relation

$$c_{H^+} c_{OH^-} = K_w \times 1 \ mol^2 dm^{-6} \tag{5-70}$$

where $K_w \approx 10^{-14}$.

Now, the electroneutrality condition, including the two additional species H+ and OH-, reads

$$c_{H^+} - c_{OH^-} + \sum_{i=1}^{N} z_i c_i = 0 \tag{5-71}$$

Combining these two equations results in the following algebraic expressions for the concentrations of H+ and OH-.

$$c_{H^+} = -\frac{\Sigma}{2} + \sqrt{\frac{\Sigma^2}{4} + K_w \times 1 \ mol^2 dm^{-6}} \tag{5-72}$$

and

$$c_{OH^-} = \frac{\Sigma}{2} + \sqrt{\frac{\Sigma^2}{4} + K_w \times 1 \ mol^2 dm^{-6}} \tag{5-73}$$

where

$$\Sigma = \sum_{i=1}^{N} z_i c_i \tag{5-74}$$

MASS BALANCE EQUATIONS FOR DISSOCIATION SPECIES

Assume a set of species Si describing k dissociation steps from

$$S_k^{z_0+k} \leftrightarrow S_{k-1}^{z_0+k-1} + H^+ \qquad K_{a,1} = \frac{[H^+][S_{k-1}^{z_0+k-1}]}{[S_k^{z_0+k}]} \qquad (5\text{-}75)$$

to

$$S_k^{z_0+1} \leftrightarrow S_0^{z_0} + H^+ \qquad K_{a,k} = \frac{[H^+][S_0^{z_0}]}{[S_1^{z_0+1}]} \qquad (5\text{-}76)$$

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 jth dissociation reaction. The brackets "[ ]" here represent 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

$$[S_m] = \frac{[H]^{m-l}[S_l]}{\displaystyle\prod_{j=k-m+1}^{k-l} K_{a,j}} \qquad (5\text{-}77)$$

if $m > l$ and

$$[S_m] = [H]^{m-l}[S_l] \prod_{j=k-l+1}^{k-m} K_{a,j} \qquad (5\text{-}78)$$

if $l > m$.

Setting $m = i$ and denoting the flux of species i by $\mathbf{N}_i$ using equation Equation 5-65, the mass balance equation for the concentration c_i of each subspecies i in the dissociation chain is

$$\frac{\delta c_i}{\delta t} + \nabla \cdot \mathbf{N}_i = R_{eq,i,k-i} - R_{eq,i,k-i+1} + R_i \qquad (5\text{-}79)$$

where $R_{eq,i,j}$ is the reaction source stemming from the jth dissociation step (with $R_{eq,i,k+1} = 0$), 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

$$\sum_{i=0}^{k}\left(\frac{\delta c_i}{\delta t} + \nabla \cdot \mathbf{N}_i\right) = \sum_{i=0}^{k} R_i \qquad (5\text{-}80)$$

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, you 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:

$$\mathbf{N}_i = -D\nabla c_i - \bar{z} u_m F c_i \nabla \phi_l + \mathbf{u} c_i \qquad (5\text{-}81)$$

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 you need 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

$$\mathbf{i}_l = \ldots - F(\bar{z} D_i \nabla c_i + \overline{z^2} u_m c_i \nabla \phi_l) \qquad (5\text{-}82)$$

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

$$\overline{\nu^2} = -c_{H^+}\frac{d}{dc_{H^+}}\bar{\nu} + \bar{\nu}^2 \qquad (5\text{-}83)$$

And from this you can derive the average squared charge according to

$$\overline{z^2} = -c_{H^+}\frac{d}{dc_{H^+}}\bar{\nu} + \bar{z}^2 = -c_{H^+}\frac{d}{dc_{H^+}}\bar{z} + \bar{z}^2 \qquad (5\text{-}84)$$

DIFFUSIVITY-MOBILITY RELATIONS

The Stokes radius r of a molecule is related to the diffusivity according to

$$r = \frac{kT}{6\pi\mu D} \tag{5-85}$$

where is the μ (SI unit: Pa·s) is the dynamic viscosity and k the Boltzmann constant.

For small molecules, there is the frequently used Nernst–Einstein relation between the diffusivity and the mobility

$$u_m = \frac{D}{RT} \tag{5-86}$$

For larger molecules, such as proteins, the mobility may instead be calculated based on the Debye–Hückel–Henry expression (Ref. 2) according to

$$u_m = \frac{ef(\kappa r)}{6\pi\mu F(1 + \kappa r)} = \frac{Df(\kappa r)}{RT(1 + \kappa r)} \tag{5-87}$$

where κ (1/m) is the Debye parameter, which depends on the ionic strength of the solution, is defined for ideal solutions as

$$\kappa^2 = \frac{2e^2 N_A}{\varepsilon\varepsilon_0 kT} \sum_{i=1}^{N} z_i^2 c_i \tag{5-88}$$

where ε is the dielectric constant of the fluid and ε_0 the permittivity of free space. (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 $1/\kappa$, 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

$$\kappa^2 = \frac{2e^2 N_A}{\varepsilon\varepsilon_0 kT} \left(\sum_{i=1}^{N-M} z_i^2 c_i + \sum_{i=N-M+1}^{N} \text{abs}(z_i)c_i \right) \tag{5-89}$$

REFERENCES

1. R.A. Mosher, D.A. Saville, and W. Thormann, *The Dynamics of Electrophoresis*, VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1992.

2. R.A. Mosher, P. Gebauer, J. Caslavska, and W. Thormann, "Computer Simulation and Experimental Validation of the Electrophoretic Behavior of Proteins. 2. Model Improvement and Application to Isotachophoresis," *Anal. Chem.*, 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:

$$\frac{\partial c_{s,i}}{\partial t} = -\nabla_t \cdot \mathbf{N}_{t,i} + R_{s,i} \tag{5-90}$$

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:

$$R_{b,\,\mathrm{tot}} = \sum_k R_{b,\,k}$$

$$r_{b,\,\mathrm{tot}} = \sum_k r_{b,\,k}$$

$$v_{b,\,\mathrm{tot}} = \sum_k v_{b,\,k}$$

FRACTIONAL RATES AND VELOCITY

The fractional deposition rates are calculated by:

$$R_{b,\,\mathrm{frac},\,k} = \frac{R_{b,\,k}}{R_{b,\,\mathrm{tot}}}$$

$$r_{b,\,\mathrm{frac},\,k} = \frac{r_{b,\,k}}{r_{b,\,\mathrm{tot}}}$$

$$v_{b,\,\mathrm{frac},\,k} = \frac{v_{b,\,k}}{v_{b,\,\mathrm{tot}}}$$

> 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: $\mathrm{mol/m^2}$), for species k is governed by the equation:

$$\frac{\partial c_{b,\,k}}{\partial t} = R_{b,\,k} \tag{5-91}$$

The bulk concentration in mass basis, $m_{b,k}$ (SI unit: $\mathrm{kg/m^2}$) 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 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 5-90 and Equation 5-91, 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 5-90 and Equation 5-91, 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 Coupling of Mass Transport to Electrochemical Reactions

When relating the species fluxes at an electrode surface to the electrical currents, the general chemical reaction formula
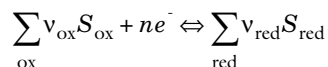
$$\sum_{\text{ox}} v_{\text{ox}} S_{\text{ox}} + ne^- \Leftrightarrow \sum_{\text{red}} v_{\text{red}} S_{\text{red}}$$

is used to define the stoichiometric coefficients, v_i, with v_i being positive (v_{red}) for products and negative (v_{ox}) for the reactants in a reduction reaction. The number of participating electrons, n, is always positive.

In this section:

- Molar Sources and Sinks
- Mass Sources and Sinks

Molar Sources and Sinks

The molar species fluxes, N_i (SI unit: mol/(m^2·s)), perpendicular to an electrode-electrolyte interface are calculated by summing all the flux contributions from the electrode reactions, of index m, according to Faraday's law:

$$N_i = \sum_m \frac{v_{i,m} i_m}{n_m F}$$

where i_m is the local current density (SI unit: A/m^2) of the electrochemical reaction, n_m the number of participating electrons and F (SI unit: C/mol) is *Faraday's constant*.

The molar species flux, N_i, is obtained from normal component of the molar species flux vector over the electrode-electrolyte interface:

$$N_i = \mathbf{N}_i \cdot \mathbf{n}$$

where $\mathbf{n}$ is the normal vector of the boundary pointing into the domain.

For a porous electrode, the electrochemical reactions result in species source terms calculated from:

$$R_{i,\,\text{molar}} = -\sum_m a_{v,\,m} \frac{\nu_{i,\,m} i_m}{n_m F}$$

where $a_{v,m}$, (SI unit: m^2/m^3) is the specific surface area.

Mass Sources and Sinks

To compute the mass flux of a species, $\mathbf{n}_i$ (SI unit: $\text{kg}/(\text{m}^2 \cdot \text{s})$), the molar flux is multiplied by the molar mass, M_i (SI unit: kg/mol), resulting in

$$\mathbf{n}_i \cdot \mathbf{n} = M_i N_i$$

for a mass flux boundary, and

$$R_{i,\,\text{mass}} = M_i R_{i,\,\text{molar}}$$

for a porous source term.

Theory for the Reacting 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
- Nonisothermal Reacting Flow
- References for the Reacting Flow Interfaces

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:

$$\rho \frac{\omega_i - \text{nojac}(\omega_i)}{\Delta \tilde{t}}$$

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 $\Delta \tilde{t}$ 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 $\Delta \tilde{t}$.

📝	For a description of the pseudo time step term for the Navier–Stokes equations and the pseudo time step see 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

$$\mathbf{n} \cdot (\mathbf{j}_i + \rho \omega_i \mathbf{u}) = r_{s,i} M_i \qquad (5\text{-}92)$$

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 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:

$$\mathbf{n} \cdot \rho \mathbf{u}_s = \sum_{i=1}^{N} r_{s,i} M_i \qquad (5\text{-}93)$$

referred to as the Stefan velocity, here denoted $\mathbf{u}_s$. To reach Equation 5-93 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 5-93 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:

$$\mathbf{n} \cdot \rho \mathbf{u}_s = \sum_{i=1}^{N} \mathbf{n} \cdot (\mathbf{j}_{0,i} + \rho \omega_{0,i} u) \qquad (5\text{-}94)$$

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

$$\mathbf{n} \cdot \mathbf{u}_s = \frac{\displaystyle\sum_{i=1}^{N} \mathbf{n} \cdot \mathbf{j}_{0,i}}{\rho\left(1 - \displaystyle\sum_{i} \omega_{i,0}\right)} \tag{5-95}$$

Using a Reacting Flow interface, the Stefan velocity, defined in the manner of Equation 5-95, 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 feature (in Transport of Concentrated Species), the default (Automatic) reaction rate used by the feature is based on the mass action law. Consider a general reaction belonging to a set of j reactions and involving i species:

$$aA + bB + \cdots \underset{k_j^r}{\overset{k_j^f}{\rightleftharpoons}} xX + yY + \cdots \tag{5-96}$$
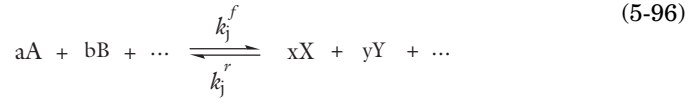
For such a reaction set, the reaction rates r_j (SI unit: mol/(m³·s)), can be described by the mass action law:

$$r_j = k_j^f \prod_{i \,\in\, \text{react}} c_i^{-\nu_{ij}} - k_j^r \prod_{i \,\in\, \text{prod}} c_i^{\nu_{ij}} \tag{5-97}$$

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/m³). 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:

$$k = A T^n \exp\left(-\frac{E}{R_g T}\right)$$

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 $(\text{m}^3/\text{mol})^{\alpha-1}/\text{s}$, where α is the order of the reaction (with respect to the concentrations).

Nonisothermal Reacting Flow

When a Chemistry interface and a Heat Transfer interface are used in the Nonisothermal Reacting Flow multiphysics coupling, the heat equation is modified to account for reactions and diffusion.

In presence of chemical reactions, the enthalpy (SI unit: J/kg) is a function of temperature, pressure and the mixture composition. For a mixture of N components, the mass fractions verify the condition $\omega_1 + \ldots + \omega_N = 1$. Therefore the enthalpy is a function of the temperature, pressure, and only $N-1$ mass fractions:

$$\hat{H} = \hat{H}(T, p, \omega_1, \ldots, \omega_{N-1})$$

Assuming the same velocity for the convection term of all components, the mass fractions follow the equation:

$$\rho\left(\frac{\partial}{\partial t}(\omega_i) + (\mathbf{u} \cdot \nabla)\omega_i\right) = -\nabla \cdot \mathbf{j}_i + R_i$$

On the other hand, using the chain rule, the enthalpy variation is written:

$$\rho\frac{D\hat{H}}{Dt} = \rho\frac{\partial\hat{H}}{\partial T}\bigg|_{p,\,\omega_j}\frac{DT}{Dt} + \rho\frac{\partial\hat{H}}{\partial p}\bigg|_{T,\,\omega_j}\frac{Dp}{Dt} + \rho\sum_{i=1}^{N-1}\frac{\partial\hat{H}}{\partial\omega_i}\bigg|_{T,\,p,\,\omega_{j\neq i}}\frac{D\omega_i}{Dt}$$

which can be rewritten using the partial molar enthalpies:

$$\bar{H}_i = \frac{\partial\hat{H}}{\partial n_i}\bigg|_{T,\,p,\,n_{j\neq i}}$$

$$\rho \frac{D\hat{H}}{Dt} = \rho \frac{\partial \hat{H}}{\partial T}\bigg|_{p,\,\omega_j} \frac{DT}{Dt} + \rho \frac{\partial \hat{H}}{\partial p}\bigg|_{T,\,\omega_j} \frac{Dp}{Dt} + \sum_{i=1}^{N} \frac{\overline{H}_i}{M_i}(-\nabla \mathbf{j}_i + R_i)$$

Additionally, the heat balance equation in terms of internal energy is written:

$$\rho \frac{DE}{Dt} = -\nabla \cdot \mathbf{q} + Q_{vd} + Q$$

where Q_{vd} is the heat source from viscous dissipation, and Q represents additional sources. The heat flux $\mathbf{q}$ consists in a term of conduction and a term of diffusion:

$$\mathbf{q} = \mathbf{q}_{cond} + \mathbf{q}_{diff} = -k\nabla T + \sum_{i=1}^{N} \frac{\overline{H}_i}{M_i}\mathbf{j}_i$$

Enthalpy and internal energy are linked through the formula $E = \hat{H} - \frac{p}{\rho}$, we can thus rewrite the heat balance equation in terms of enthalpy:

$$\rho \frac{\partial \hat{H}}{\partial T}\bigg|_{p,\,\omega_j} \frac{DT}{Dt} + \left(\rho \frac{\partial \hat{H}}{\partial p}\bigg|_{T,\,\omega_j} - 1\right)\frac{Dp}{Dt} + \sum_{i=1}^{N} \frac{\overline{H}_i}{M_i}(-\nabla \mathbf{j}_i + R_i) = -\nabla \cdot \mathbf{q} + Q_{vd} + Q$$

Introducing the heat capacity at constant pressure C_p (SI unit: J/(kg·m^3)), and the coefficient of thermal expansion α_p (SI unit: 1/K) gives:

$$\rho C_p \frac{DT}{Dt} - \alpha_p T \frac{Dp}{Dt} + \sum_{i=1}^{N} \frac{\overline{H}_i}{M_i}(-\nabla \mathbf{j}_i + R_i) = -\nabla \cdot \mathbf{q} + Q_{vd} + Q$$

The term with the pressure derivative is the work of pressure forces Q_p. The enthalpy variation due to the gradient of species mass flux can be partly simplified with the diffusion part of the heat flux. The heat source of reaction can be written in terms of enthalpies of reaction H_i instead of partial enthalpies (see Ref. 1). The temperature derivative term can be expanded to make the convective term appear. We finally obtain the temperature equation for a free flow with N species and M reactions:

$$\rho C_p\left[\frac{\partial T}{\partial t} + (\mathbf{u} \cdot \nabla)T\right] + \nabla \cdot (-k\nabla T) = Q_{diff} + Q_{react} + Q_{vd} + Q_p + Q$$

$$Q_{\text{diff}} = -\sum_{i=1}^{N} \mathbf{j}_i \cdot \nabla\left(\frac{\overline{H}_i}{M_i}\right)$$

$$Q_{\text{react}} = -\sum_{i=1}^{M} H_i r_i$$

$$Q_{\text{vd}} = (-p\mathbf{I} + \tau):\nabla\mathbf{u}$$

$$Q_p = \alpha_p T\left[\frac{\partial p}{\partial t} + (\mathbf{u} \cdot \nabla)p\right]$$

For reacting flows moving through the interstices of a porous medium, the heat sources of reaction and diffusion are only accounted for the temperature of the fluid phase. While the porosity is already accounted for in the diffusion term through the mass flux, the heat source of reaction has to be multiplied by the porosity. Also, in presence of a porous catalyst, both reactions in the bulk and reactions at the surface are accounted for in the reaction source term:

$$Q_{\text{react}} = -\varepsilon_p \sum_{i=1}^{M_{\text{bulk}}} H_i r_i - S_{\text{area}} \sum_{i=1}^{M_{\text{surf}}} H_i^s r_i^s$$

where ε_p is the porosity of the medium (SI unit: 1), S_{area} is the specific surface area (SI unit: 1/m), and r_i^s is the surface reaction rate (SI unit: mol/(m^2·s)).

An additional source term is added to model convective heat transfer between the fluid and the porous matrix to get the temperature equation for nonisothermal reacting flows in porous media:

$$\rho_f C_{p,f}\left[\frac{\partial T_f}{\partial t} + (\mathbf{u} \cdot \nabla)T_f\right] + \nabla \cdot (-k_f \nabla T_f) = Q_{\text{diff}} + Q_{\text{react}} + Q_{\text{vd}} + Q_p + Q_{s,f} + Q$$

This equation is the one that is solved when the **Porous medium type** of the Porous Medium feature is set to **Local thermal nonequilibrium**, since both fluid and porous matrix temperatures are solved separately. With the **Local thermal equilibrium** approach, the equation is written for the common temperature, and in terms of effective material properties for the time derivative term and conduction term:

$$(\rho C_p)_{\text{eff}} \frac{\partial T}{\partial t} + \rho_{\text{f}} C_{p,\,\text{f}} (\mathbf{u} \cdot \nabla) T + \nabla \cdot (-k_{\text{eff}} \nabla T) \;=\; Q_{\text{diff}} + Q_{\text{react}} + Q_{\text{vd}} + Q_p + Q$$

References for the Reacting Flow Interfaces

1. H.A. Jakobsen, *Chemical Reactor Modeling: Multiphase Reactive Flows*, Springer, 2008.

6

Fluid Flow Interfaces

This chapter describes the physics interfaces found under the **Fluid Flow** branch
(≋).

In this chapter:

- The Laminar Flow and Creeping Flow Interfaces
- The Darcy's Law Interface
- The Free and Porous Media Flow, Brinkman Interface
- The Free and Porous Media Flow, Darcy Interface
- The Brinkman Equations Interface
- The Multiphase Flow in Porous Media Interface
- The Multiphase Free and Porous Media Flow Interface
- The Bubbly Flow Interface
- The Mixture Model Interface
- The Euler-Euler Model Interface
- Theory for the Laminar Flow and Creeping Flow Interfaces
- Theory for the Darcy's Law Interface
- Theory for the Free and Porous Media Flow, Brinkman Interface

- Theory for the Free and Porous Media Flow, Darcy Interface
- Theory for the Brinkman Equations Interface
- Theory for the Multiphase Flow in Porous Media Interface
- Theory for the Bubbly Flow Interface
- Theory for the Mixture Model Interface
- Theory for the Euler-Euler Interface
- Theory for the Coupling of Fluid Flow to Electrochemical Reactions

The Laminar Flow and Creeping Flow Interfaces

In this section:

- The Creeping Flow Interface
- The Laminar Flow Interface
- The Bubbly Flow Interface

🔍	• Theory for the Coupling of Fluid Flow to Electrochemical Reactions

In the *COMSOL Multiphysics Reference Manual*, see Table 2-4 for links to common sections such as **Discretization**, **Consistent Stabilization**, **Inconsistent Stabilization**, and **Advanced Settings** sections, some of them accessed by clicking the **Show** button (👁) and choosing the applicable option. You can also search for information: press F1 to open the **Help** window or Ctrl+F1 to open the **Documentation** window.

The Creeping Flow Interface

The **Creeping Flow (spf)** interface (≋) is used for simulating fluid flows at very low Reynolds numbers for which the inertial term in the Navier–Stokes equations can be neglected. Creeping flow, also referred to as Stokes flow, occurs in systems with high viscosity or small geometrical length scales (for example, in microfluidics and MEMS devices). The fluid can be compressible or incompressible, as well as Newtonian or non-Newtonian.

The equations solved by the Creeping Flow interface are the Stokes equations for conservation of momentum and the continuity equation for conservation of mass.

The Creeping Flow interface can be used for stationary and time-dependent analyses.

The main feature is the **Fluid Properties** node, which adds the Stokes equations and provides an interface for defining the fluid material and its properties. Except where noted below, see The Laminar Flow Interface for all other settings.

PHYSICAL MODEL

By default, the **Neglect inertial term (Stokes flow)** check box is selected. If unchecked, the inertial terms are included in the computations.

DISCRETIZATION

By default, the Creeping Flow interface uses **P2+P1** elements. Contrary to general laminar and turbulent single-phase flow simulations employing purely linear P1+P1 elements, P2+P1 elements are well suited for most creeping flow simulations but are not in general fully conservative. Full conservation properties and high accuracy is obtained by selecting P2+P2 or P3+P3 elements.

Note that P1+P1, P2+P2, and P3+P3 discretizations (the so-called equal order interpolations) require streamline diffusion to be active.

The Laminar Flow Interface

The **Laminar Flow (spf)** interface ( ) is used to compute the velocity and pressure fields for the flow of a single-phase fluid in the laminar flow regime. A flow remains laminar as long as the Reynolds number is below a certain critical value. At higher Reynolds numbers, disturbances have a tendency to grow and cause transition to turbulence. This critical Reynolds number depends on the model, but a classical example is pipe flow, where the critical Reynolds number is known to be approximately 2000.

The physics interface supports incompressible flow, weakly compressible flow (the density depends on temperature but not on pressure), and compressible flow at low Mach numbers (typically less than 0.3). It also supports flow of non-Newtonian fluids.

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.

The Laminar Flow interface can be used for stationary and time-dependent analyses. Time-dependent studies should be used in the high-Reynolds number regime as these flows tend to become inherently unsteady.

When the Laminar Flow interface is added, the following default nodes are also added in the **Model Builder**: **Fluid Properties**, **Wall** (the default boundary condition is **No slip**), and **Initial Values**. Other nodes that implement, for example, boundary conditions and volume forces, can be added from the **Physics** toolbar or from the context menu displayed when right-clicking **Laminar Flow**.

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

The **Name** is used primarily as a scope prefix for variables defined by the physics interface. Physics interface variables can be referred to 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 spf.

About the Physics Interface Label Names

The label for a single-phase flow interface (the node name in the Model Builder) is dynamic and is reset according to the turbulence model and the neglect inertial term (Stokes flow) property set at the physics interface level. The availability also depends on the software license.

If the **Neglect inertial term (Stokes flow)** check box is selected, then the Label changes to **Creeping Flow**, which is the same Label that displays when that interface is added from the Model Wizard or Add Physics window.

PHYSICAL MODEL

Compressibility

Depending of the fluid properties and the flow regime, three options are available for the **Compressibility** option. In general the computational complexity increases from **Incompressible flow** to **Weakly compressible flow** to **Compressible flow (Ma<0.3)** but the underlying hypotheses are increasingly more restrictive in the opposite direction.

When the **Incompressible flow** option (default) is selected, the incompressible form of the Navier–Stokes and continuity equations is applied. In addition, the fluid density is evaluated at the **Reference pressure level** defined in this section. The **Reference temperature** is set to 293.15 K.

The **Weakly compressible flow** option models compressible flow when the pressure dependency of the density can be neglected. When selected, the compressible form of the Navier–Stokes and continuity equations is applied. In addition, the fluid density is evaluated at the **Reference pressure level** defined in this section.

When the **Compressible flow (Ma<0.3)** option is selected, the compressible form of the Navier–Stokes and continuity equations is applied. $\text{Ma} < 0.3$ indicates that the inlet and outlet conditions, as well as the stabilization, may not be suitable for transonic and supersonic flow. For more information, see The Mach Number Limit.

Porous Media Domains

With the addition of various modules, the **Enable porous media domains** check box is available. Selecting this option, a **Fluid and Matrix Properties** node, a **Mass Source** node, and a **Forchheimer Drag** subnode are added to the physics interface. These are described for the **Brinkman Equations** interface in the respective module's documentation. The **Fluid and Matrix Properties** can be applied on all domains or on a subset of the domains.

Porous Treatment of No Slip Condition

Porous treatment of no slip condition is available when **Enable porous media domains** is activated. It controls how the **No Slip** condition on **Wall** boundaries and **Interior Wall** boundaries adjacent to **Porous Medium** should be treated. The options are **Standard no slip formulation** (default) and **Porous slip**. The latter option provides a unified treatment when the porous matrix is fully resolved as well as when it is under resolved ensuring a smooth transition between regions with different resolutions; see No Slip under Wall.

Include Gravity

When the **Include gravity** check box is selected, a global **Gravity** feature is shown in the interface model tree, and the buoyancy force is included in the Navier–Stokes equations.

Also, when the **Include gravity** check box is selected, the **Use reduced pressure** option changes the pressure formulation from using the total pressure (default) to using the reduced pressure. This option is suitable for configurations where the density changes are very small; otherwise, the default formulation can be used. For more information, see Gravity

Reference Values

Reference values are global quantities used to evaluate the density of the fluid when the **Incompressible flow** or the **Weakly compressible flow** option is selected.

Reference pressure level   There are generally two ways to include the pressure in fluid flow computations: either to use the absolute pressure $p_A=p+p_{ref}$, or the gauge pressure p. When p_{ref} is nonzero, the physics interface solves for the gauge pressure whereas material properties are evaluated using the absolute pressure. The reference pressure level is also used to define the reference density.

Reference temperature   The reference temperature is used to define the reference density.

Reference position When **Include gravity** is selected, the reference position can be defined. It corresponds to the location where the total pressure (that includes the hydrostatic pressure) is equal to the **Reference pressure level**.

DEPENDENT VARIABLES

The following dependent variables (fields) are defined for this physics interface — the **Velocity field u** and its components, and the **Pressure** p.

If required, the names of the field, component, and dependent variable can be edited. Editing the name of a scalar dependent variable changes both its field name and the dependent variable name. If a new field name coincides with the name of another field of the same type, the fields share degrees of freedom and dependent variable names. A new field name must not coincide with the name of a field of another type or with a component name belonging to some other field. Component names must be unique within a model except when two fields share a common field name.

CONSISTENT STABILIZATION

To enable this section, click the **Show More Options** button (👁) and select **Stabilization** in the **Show More Options** dialog box.

There are two *consistent stabilization methods*: **Streamline diffusion** and **Crosswind diffusion**. Usually, both check boxes for these methods are selected by default and should remain selected for optimal performance. Consistent stabilization methods do not perturb the original transport equation. Streamline diffusion must be selected when using equal-order interpolation for pressure and velocity.

Select the **Use dynamic subgrid time scale** check box to estimate the influence of temporal variations in the velocity field, instead of using the inverse time step, in the consistent stabilization terms. This check box is selected by default

Select the **Limit small time steps effect on stabilization time scale** check box to prevent loss of stabilization at small time steps.

INCONSISTENT STABILIZATION

To enable this section, click the **Show More Options** button (👁) and select **Stabilization** in the **Show More Options** dialog box.

There is usually just one *inconsistent stabilization method* — **Isotropic diffusion**. This method is equivalent to adding a term to the diffusion coefficient in order to dampen the effect of oscillations by making the system somewhat less dominated by convection. If possible, minimize the use of the inconsistent stabilization method

because by using it you no longer solve the original problem. 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 underresolved problems.

If required, select the **Isotropic diffusion** check box and enter a **Tuning parameter** δ_{id} as a scalar positive value. The default value is 0.25 (a reasonable value to start with is roughly 0.5 divided by the element order). A higher value adds more isotropic diffusion.

🔍	• Numerical Stability — Stabilization Techniques for Fluid Flow

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.

The **Use pseudo time stepping for stationary equation form** is per default set to **Automatic from physics**. This option can add pseudo time derivatives to the equation when the **Stationary equation** form is used in order to speed up convergence. Pseudo time stepping is triggered when the Laminar Flow interface is selected in some multiphysics coupling features. Set **Automatic from physics** to **On** to apply pseudo time stepping also for laminar flows. Set it to **Off** to disable pseudo time stepping completely.

When **Use pseudo time stepping for stationary equation form** is set to **Automatic from physics** or **On**, 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.

The **Use Block Navier-Stokes preconditioner** check box under **Linear solver** is available when the **Compressibility** option is set to **Incompressible flow**. When this check box is selected, the default solver for time-dependent study steps will use the Block Navier–Stokes preconditioner in iterative solvers for the velocity and pressure. Using this

preconditioner may result in shorter solution times for large time dependent problems with high Reynolds numbers.

🔍
- Pseudo Time Stepping for Laminar Flow Models
- Domain, Boundary, Pair, and Point Nodes for Single-Phase Flow
- Theory for the Coupling of Fluid Flow to Electrochemical Reactions
- Block Navier–Stokes in the *COMSOL Multiphysics Reference Manual*.

DISCRETIZATION

The default discretization for Laminar Flow is **P1+P1** elements — that is, piecewise linear interpolation for velocity and pressure. This is suitable for most flow problems.

Some higher-order interpolations are also available, and they can be cost-effective options to obtain high accuracy for flows with low Reynolds numbers.

The **P2+P2** and **P3+P3** options, the equal-order interpolation options, are the preferred higher-order options because they have higher numerical accuracy than the mixed-order options **P2+P1** and **P3+P2**. The equal-order interpolation options do, however, require streamline diffusion to be active.

▦
Flow Past a Cylinder: Application Library path **COMSOL_Multiphysics/ Fluid_Dynamics/cylinder_flow**

Domain, Boundary, Pair, and Point Nodes for Single-Phase Flow

The following nodes, listed in alphabetical order, are 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).

- Boundary Stress
- Flow Continuity
- Fluid Properties
- Gravity
- Initial Values
- Inlet
- Line Mass Source[1]
- Open Boundary
- Outlet

- Periodic Flow Condition
- Point Mass Source[1]
- Porous Interface
- Pressure Point Constraint
- Symmetry
- Volume Force
- Wall

[1] A feature that may require an additional license

	For 2D axisymmetric components, COMSOL Multiphysics takes the axial symmetry boundaries (at $r = 0$) into account and adds an **Axial Symmetry** node that is valid on the axial symmetry boundaries only.

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 a detailed overview of the functionality available in each product, visit https://www.comsol.com/products/specifications/

Fluid Properties

The **Fluid Properties** node adds the momentum and continuity equations solved by the physics interface, except for volume forces, which are added by the Volume Force feature. The node also provides an interface for defining the material properties of the fluid.

MODEL INPUTS

Fluid properties, such as density and viscosity, can be defined through user inputs, variables, or by selecting a material. For the latter option, additional inputs, for example temperature or pressure, may be required to define these properties.

Temperature

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.

Absolute Pressure

This input appears when a material requires the absolute pressure as a model input. The absolute pressure is used to evaluate material properties, but it also relates to the value of the calculated pressure field. There are generally two ways to calculate the pressure when describing fluid flow: either to solve for the absolute pressure or for a pressure (often denoted gauge pressure) that relates to the absolute pressure through a reference pressure.

The choice of pressure variable depends on the system of equations being solved. For example, in a unidirectional incompressible flow problem, the pressure drop over the modeled domain is probably many orders of magnitude smaller than the atmospheric pressure, which, when included, may reduce the stability and convergence properties of the solver. In other cases, such as when the pressure is part of an expression for the gas volume or the diffusion coefficients, it may be more convenient to solve for the absolute pressure.

The default **Absolute pressure** p_A is $p + p_{ref}$, where p is the dependent pressure variable from the Navier–Stokes or RANS equations, and p_{ref} is from the user input defined at the physics interface level. When p_{ref} is nonzero, the physics interface solves for a gauge pressure. If the pressure field instead is an absolute pressure field, p_{ref} should be set to 0.

The **Absolute pressure** field can be edited by clicking **Make All Model Inputs Editable**
(![icon]) and entering the desired value in the input field.

🔍   Model Inputs and Multiphysics Couplings in the *COMSOL Multiphysics Reference Manual*

FLUID PROPERTIES

Density

The density can either be specified by a material, or by a **User defined** expression. The density in a material can depend on temperature and pressure, and these dependencies are automatically replaced by p_{ref} for weakly compressible flows and p_{ref} and T_{ref} for incompressible flows (as specified by the **Compressibility** setting at the physics interface level). If density variations with respect to pressure are to be included in the computations, **Compressibility** must be set to compressible. Any dependencies in the density on quantities other than temperature and pressure must be consistent with the **Compressibility** setting at the interface level.

Dynamic Viscosity

The **Dynamic viscosity** μ describes the relationship between the shear rate and the shear stresses in a fluid. Intuitively, water and air have low viscosities, and substances often described as thick (such as oil) have higher viscosities.

Volume Force

The **Volume Force** node specifies the volume force $\mathbf{F}$ on the right-hand side of the momentum equation.

$$\rho\frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u}\cdot\nabla)\mathbf{u} = \nabla\cdot\left[-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla\cdot\mathbf{u})\mathbf{I}\right] + \mathbf{F}$$

If several volume-force nodes are added to the same domain, then the sum of all contributions are added to the momentum equation.

Initial Values

The initial values serve as initial conditions for a transient simulation or as an initial guess for a nonlinear solver in a stationary simulation. Note that for a transient compressible-flow simulation employing a material for which the density depends on

the pressure (such as air), discontinuities in the initial values trigger pressure waves even when the Mach number is small. The pressure waves must be resolved and this puts a restriction on the time step.

INITIAL VALUES

Initial values or expressions should be specified for the **Velocity field u** and the **Pressure** *p*.

When **Include gravity** is selected and **Use reduced pressure** not selected in the interface **Physical model** section, the **Compensate for hydrostatic pressure approximation** (named **Compensate for hydrostatic pressure** for compressible flows) check box is available and selected by default. When it is selected, the hydrostatic pressure is automatically added to the pressure entered in *p* user input.

Wall

The **Wall** node includes a set of boundary conditions describing fluid-flow conditions at stationary, moving, and leaking walls. For turbulent flow, the description may involve wall functions and asymptotic expressions for certain turbulence variables.

BOUNDARY CONDITION

Select a **Boundary condition** for the wall.

- No Slip
- Slip
- Leaking Wall
- Navier Slip

No Slip

No slip is the default boundary condition to model solid walls. A no-slip wall is a wall where the fluid velocity relative to the wall velocity is zero. For a stationary wall that means that $\mathbf{u} = 0$.

The option for **Porous treatment of no slip condition** is available when **Enable porous media domains** is activated in the **Physical Model** section in the settings for the main physics interface node. It specifies how **Wall** boundaries and **Interior Wall** boundaries adjacent to porous domains are treated. When **Standard no slip formulation** is chosen, a common no slip condition is applied on all solid walls. When the default **Porous slip** is chosen, a blending analytic expression is instead applied on the corresponding wall boundaries adjacent to the porous medium domain. It results in a no slip condition in case the porous length scale is fully resolved by the mesh and a slip condition in the

opposite limit when the mesh is much coarser than the porous scale. A smooth transition between these limits is ensured. Note that the interpretation and usage of nonzero slip at the wall is the same as in the **Navier slip** boundary condition. By default, **Velocity formulation** is on and the treatment is based on an approximate reconstruction of the far field pressure gradient using the slip velocity at the wall. If the **Pressure-gradient formulation** is chosen, the local pressure gradient at the wall is employed.

Slip

The **Slip** option prescribes a no-penetration condition, $\mathbf{u}\cdot\mathbf{n} = 0$. It is implicitly assumed that there are no viscous effects at the slip wall and hence, no boundary layer develops. From a modeling point of view, this can be a reasonable approximation if the main effect of the wall is to prevent fluid from leaving the domain.

Leaking Wall

This boundary condition may be used to simulate a wall where fluid is leaking into or leaving the domain with the velocity $\mathbf{u} = \mathbf{u}_l$ through a perforated wall. The components of the **Fluid velocity $\mathbf{u}_l$** on the leaking wall should be specified.

Navier Slip

This boundary condition enforces no-penetration at the wall, $\mathbf{u} \cdot \mathbf{n}_{wall} = 0$, and adds a tangential stress

$$\mathbf{K}_{nt} = -\frac{\mu}{\beta}\mathbf{u}_{slip}$$

where $\mathbf{K}_{nt} = \mathbf{K}_n - (\mathbf{K}_n \cdot \mathbf{n}_{wall})\mathbf{n}_{wall}$, $\mathbf{K}_n = \mathbf{K}\mathbf{n}_{wall}$, and $\mathbf{K}$ is the viscous stress tensor. β is a slip length, and $\mathbf{u}_{slip} = \mathbf{u} - (\mathbf{u} \cdot \mathbf{n}_{wall})\mathbf{n}_{wall}$ is the velocity tangential to the wall.

The **Slip length** setting is per default set to **Factor of minimum element length**. The slip length β is then defined as $\beta = f_h h_{min}$, where h_{min} is the smallest element side and f_h is a user input. Select **User defined** from the **Slip length** selection list in order to manually prescribe β (SI unit: m).

In cases where the wall movement is nonzero, check **Account for the translational wall velocity in the friction force** to use $\mathbf{u} - \mathbf{u}_{bnd} - ((\mathbf{u} - \mathbf{u}_{bnd}) \cdot \mathbf{n}_{wall})\mathbf{n}_{wall}$ instead of $\mathbf{u}_{slip}$ in the friction force.

The Navier slip option is not available when selecting a turbulence model.

WALL MOVEMENT

This section contains controls to describe the wall movement relative to the lab (or spatial) frame.

The **Translational velocity** setting controls the translational wall velocity, $\mathbf{u}_{tr}$. The list is per default set to **Automatic from frame**. The physics automatically detects if the spatial frame moves. This can for example happen if an ALE interface is present in the model component. If there is no movement $\mathbf{u}_{tr} = \mathbf{0}$. If the frame moves, $\mathbf{u}_{tr}$ becomes equal to the frame movement. $\mathbf{u}_{tr}$ is accounted for in the actual boundary condition prescribed in the **Boundary condition** section.

Select **Zero (Fixed wall)** from **Translational velocity** selection list to prescribe $\mathbf{u}_{tr} = \mathbf{0}$.

Select **Manual** from **Translational velocity** selection list in order to manually prescribe **Velocity of moving wall**, $\mathbf{u}_{tr}$. This can for example be used to model an oscillating wall where the magnitude of the oscillations are very small compared to the rest of the model. Specifying translational velocity manually does not automatically cause the associated wall to move. An additional Moving Mesh node needs to be added from Definitions to physically track the wall movement in the spatial reference frame.

The **Sliding wall** option is appropriate if the wall behaves like a conveyor belt with the surface sliding in a tangential direction. A velocity is prescribed at the wall and the boundary itself does not have to actually move relative to the reference frame.

- For 3D components, values or expressions for the **Velocity of sliding wall $\mathbf{u}_w$** should be specified. If the velocity vector entered is not in the plane of the wall, COMSOL Multiphysics projects it onto the tangential direction. Its magnitude is adjusted to be the same as the magnitude of the vector entered.

- For 2D components, the tangential direction is unambiguously defined by the direction of the boundary. For this reason, the sliding wall boundary condition has different definitions in different space dimensions. A single entry for the **Velocity of the tangentially moving wall** U_w should be specified in 2D.

CONSTRAINT SETTINGS

This section is displayed by clicking the **Show More Options** button (👁) and selecting **Advanced Physics Options** in the **Show More Options** dialog box. The **Constraints** settings can be set to **Automatic**, **Pointwise constraints**, **Nitsche constraints**, or **Weak constraints**. **Mixed constraints** can be selected when imposing a no slip condition exactly.

Depending on the constraint method selected, the following settings are available:

- **Apply reaction terms on** can be set to **Individual dependent variables** (default) or **All physics (symmetric)**. This setting is not available when **Nitsche constraints** is selected.

- Select **Elemental** (default) or **Nodal** under **Constraint method**. This setting is not available for **Nitsche constraints** or **Weak constraints**.

🔍	• Theory for the Wall Boundary Condition • The Moving Mesh Interface in the *COMSOL Multiphysics Reference Manual*

Inlet

This condition should be used on boundaries for which there is a net flow into the domain. To obtain a numerically well-posed problem, it is advisable to also consider the Outlet conditions when specifying an Inlet condition. For example, if the pressure is specified at the outlet, the velocity may be specified at the inlet, and vice versa. Specifying the velocity vector at both the inlet and the outlet may cause convergence difficulties.

BOUNDARY CONDITION

The available **Boundary condition** options for an inlet are **Velocity, Fully developed flow**, and **Pressure**. After selecting a **Boundary Condition** from the list, a section with the same or a similar name displays underneath. For example, if **Velocity** is selected, a **Velocity** section, where further settings are defined, is displayed.

VELOCITY

The **Normal inflow velocity** is specified as $\mathbf{u} = -\mathbf{n}U_0$, where $\mathbf{n}$ is the boundary normal pointing out of the domain and U_0 is the normal inflow speed.

The **Velocity field** option sets the velocity vector to $\mathbf{u} = \mathbf{u}_0$. The components of the inlet velocity vector $\mathbf{u}_0$ should be defined for this choice.

PRESSURE CONDITIONS

This option specifies the normal stress, which in most cases is approximately equal to the pressure.

- For incompressible flow, the **Pressure** list has two options, **Static** and **Total**. For weakly compressible and compressible flow, the static pressure should be specified in the text field.

  - If **Pressure** is **Static,** and the reference pressure p_{ref}, defined at the physics interface level, is equal to 0, the value of the pressure p_0, at the boundary, is the absolute pressure. Otherwise, p_0 is the relative pressure at the boundary.

  - If **Pressure** is **Total**, the **Average** check box is available and cleared by default to prescribe the total pressure pointwise. If it is selected, the averaged total pressure is imposed in the weak forms instead.

  When **Include gravity** is selected and **Use reduced pressure** not selected in the interface **Physical model** section, the **Compensate for hydrostatic pressure approximation** (named **Compensate for hydrostatic pressure** for incompressible flows) check box is available and selected by default. When it is selected, the hydrostatic pressure is automatically added to the pressure entered in p_0 user input.

- The **Suppress backflow** option adjusts the inlet pressure locally in order to reduce the amount of fluid exiting the domain through the boundary. If you clear the suppress backflow option, the inlet boundary can become an outlet depending on the pressure field in the rest of the domain.

- **Flow direction** controls in which direction the fluid enters the domain.

  - For **Normal flow**, it prescribes zero tangential velocity component.

  - For **User defined**, an **Inflow velocity direction** $\mathbf{d_u}$ (dimensionless) should be specified. The magnitude of $\mathbf{d_u}$ does not matter, only the direction. $\mathbf{d_u}$ must point into the domain.

MASS FLOW

The mass flow at an inlet can be specified by the **Mass flow rate**, the **Pointwise mass flux**, the **Standard flow rate**, or the **Standard flow rate (SCCM)**.

The **Apply condition on each disjoint selection separately** check box is selected per default. When this setting is selected, the mass flow condition is applied separately on each disjoint selection. If this option is not selected, the condition is applied over the whole feature selection. The **Apply condition on each disjoint selection separately** should be disabled only if the flow conditions are known to be identical on each disjoint boundary.

Mass Flow Rate

The **Mass flow rate** option sets the integrated mass flow over the boundary selection, the **Normal mass flow rate** to a specific value, m. The mass flow is assumed to be parallel to the boundary normal, and the tangential flow velocity is set to zero.

For 2D components, the **Channel thickness** d_{bc} is used to define the area across which the mass flow occurs. This setting is not applied to the whole model. Line or surface integrals of the mass flow over the boundary evaluated during postprocessing or used in integration coupling operators do not include this scaling automatically. Such results should be appropriately scaled when comparing them with the specified mass flow.

Pointwise Mass Flux

The **Pointwise mass flux** sets the mass flow parallel to the boundary normal. The tangential flow velocity is set to zero. The mass flux is a model input, which means that COMSOL Multiphysics can take its value from another physics interface when available. When **User defined** is selected a value or function M_f should be specified for the **Mass flux**.

Standard Flow Rate

The **Standard flow rate** Q_{sv} sets a standard volumetric flow rate, according to the SEMI standard E12-0303. The mass flow rate is specified as the volumetric flow rate of a gas at standard density — the **Mean molar mass** M_n divided by a **Standard molar volume** V_m (that is, the volume of one mole of a perfect gas at standard pressure and standard temperature). The flow occurs across the whole boundary in the direction of the boundary normal and is computed by a surface (3D) or line (2D) integral. The tangential flow velocity is set to zero.

The standard density can be defined directly, or by specifying a standard pressure and temperature, in which case the ideal gas law is assumed. The options in the **Standard flow rate defined by** list are:

- **Standard density**, for which the **Standard molar volume** V_m should be specified.
- **Standard pressure and temperature**, for which the **Standard pressure** P_{st} and the **Standard temperature** T_{st} should be defined.

For 2D components, the **Channel thickness** d_{bc} is used to define the area across which the mass flow occurs. This setting is not applied to the whole model. Line or surface integrals of the mass flow over the boundary evaluated during postprocessing or used in integration coupling operators do not include this scaling automatically. Such results should be appropriately scaled when comparing them with the specified mass flow.

The **Standard flow rate (SCCM)** boundary condition is equivalent to the **Standard flow rate** boundary condition, except that the flow rate is entered directly in SCCMs (standard cubic centimeters per minute) without the requirement to specify units. Here, the dimensionless **Number of SCCM units** Q_{sccm} should be specified.

FULLY DEVELOPED FLOW

The **Fully developed flow** option adds contributions to the inflow boundary, which force the flow toward the solution for a fully developed channel flow. The channel can be thought of as a virtual extrusion of the inlet cross section. The inlet boundary must hence be flat in order for the fully developed flow condition to work properly. In 2D axisymmetric models, the inlet normal must be parallel to the symmetry axis.

Select an option to control the flow rate at the inlet:

- **Average velocity**, U_{av}.
- **Flow rate**, V_0. Two-dimensional models also require an **Entrance thickness**, D_z, which is the out-of-plane thickness of the extruded entrance channel.
- **Average pressure**, P_{av}. Note that P_{av} is the average pressure on the inflow boundary.

The **Apply condition on each disjoint selection separately** check box is selected per default. When this setting is selected, the fully developed flow condition is applied separately on each disjoint selection. If this option is not selected, the condition is applied over the whole feature selection. The **Apply condition on each disjoint selection separately** should be disabled only if the flow conditions are known to be identical on each disjoint boundary.

The fully developed flow condition requires any volume force to be approximately aligned with the normal of the inlet boundary. The exception is gravity when the **Include gravity** setting is selected in the physics interface settings. Unless **Use reduced pressure** is also selected, an option to **Compensate for hydrostatic pressure** or **Compensate for hydrostatic pressure approximation** becomes available. It is selected per default and should only be deselected if the inlet normal is aligned with the gravity force and you want to specify an average pressure that includes the hydrostatic pressure.

This section is displayed by clicking the **Show** button (☞) and selecting **Advanced Physics Options**.

⊙	• Prescribing Inlet and Outlet Conditions • Normal Stress Boundary Condition

⊙	Fully Developed Flow (Inlet)

Outlet

This condition should be used on boundaries for which there is a net outflow from the domain. To obtain a numerically well-posed problem, it is advisable to also consider the Inlet conditions when specifying an Outlet condition. For example, if the velocity is specified at the inlet, the pressure may be specified at the outlet, and vice versa. Specifying the velocity vector at both the inlet and the outlet may cause convergence difficulties. Selecting appropriate outlet conditions for the Navier–Stokes equations is a nontrivial task. Generally, if there is something interesting happening at an outflow boundary, the computational domain should be extended to include this phenomenon.

BOUNDARY CONDITION

The available **Boundary condition** options for an outlet are **Pressure, Fully developed flow**, and **Velocity**.

PRESSURE CONDITIONS

This option specifies the normal stress, which in most cases is approximately equal to the pressure. The tangential stress component is set to zero.

- For incompressible flow, the **Pressure** list has two options, **Static** and **Total**. For weakly compressible and compressible flow, the static pressure should be specified in the text field.

    - If **Pressure** is **Static,** and the reference pressure p_{ref}, defined at the physics interface level, is equal to 0, the value of the pressure p_0, at the boundary, is the absolute pressure. Otherwise, p_0 is the relative pressure at the boundary.

    - If **Pressure** is **Total**, the **Average** check box is available and selected by default to prescribed the averaged total pressure in the weak forms. If it is cleared, the total pressure is imposed pointwise.

When **Include gravity** is selected and **Use reduced pressure** not selected in the interface **Physical model** section, the **Compensate for hydrostatic pressure approximation** (named **Compensate for hydrostatic pressure** for incompressible flows) check box is available and selected by default. When it is selected, the hydrostatic pressure is automatically added to the pressure entered in p_0 user input.

- The **Normal flow** option changes the no tangential stress condition to a no tangential velocity condition. This forces the flow to exit (or enter) the domain perpendicularly to the outlet boundary.

- The **Suppress backflow** check box is selected by default. This option adjusts the outlet pressure in order to reduce the amount of fluid entering the domain through the boundary.

VELOCITY

See the **Inlet** node Velocity section for the settings.

FULLY DEVELOPED FLOW

This boundary condition is applicable when the flow exits the domain into a long pipe or channel, at the end of which a flow profile is fully developed.

The channel can be thought of as a virtual extrusion of the outlet cross section. The outlet boundary must hence be flat in order for the fully developed flow condition to work properly. In 2D axisymmetric models, the outlet normal must be parallel to the symmetry axis.

Select an option to control the flow rate at the outlet:

- **Average velocity**, U_{av}.
- **Flow rate**, V_0. Two-dimensional models also require an **Entrance thickness**, D_z, which is the out-of-plane thickness of the extruded entrance channel.
- **Average pressure**, P_{av}. Observe that P_{av} is the average pressure on the outflow.

The **Apply condition on each disjoint selection separately** check box is selected per default. When this setting is selected, the fully developed flow condition is applied separately on each disjoint selection. If this option is not selected, the condition is applied over the whole feature selection. The **Apply condition on each disjoint selection separately** should be disabled only if the flow conditions are known to be identical on each disjoint boundary.

The fully developed flow condition requires any volume force to be approximately aligned with the normal of the outlet boundary. The exception is gravity when the **Include gravity** setting is selected in the physics interface settings. Unless **Use reduced pressure** is also selected, an option to **Compensate for hydrostatic pressure** or **Compensate for hydrostatic pressure approximation** becomes available. It is selected per default and should only be deselected if the outlet normal is aligned with the gravity force and you want to specify an average pressure that includes the hydrostatic pressure.

CONSTRAINT SETTINGS

This section is displayed by clicking the **Show** button (👁) and selecting **Advanced Physics Options**.

🔍	Prescribing Inlet and Outlet Conditions

🔍	Fully Developed Flow (Outlet)

Symmetry

This node provides a boundary condition for symmetry boundaries. It should only be used when the geometry and expected solution have mirror symmetry. By using

symmetries in a model its size can be reduced by one-half or more, making this an efficient tool for solving large problems.

The **Symmetry** boundary condition prescribes no penetration and vanishing shear stresses. The boundary condition is a combination of a Dirichlet condition and a Neumann condition:

$$\mathbf{u} \cdot \mathbf{n} = 0, \qquad \left(-p\mathbf{I} + \left(\mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right)\right)\mathbf{n} = \mathbf{0}$$

$$\mathbf{u} \cdot \mathbf{n} = 0, \qquad (-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T))\mathbf{n} = \mathbf{0}$$

for the compressible and incompressible formulations. The Dirichlet condition takes precedence over the Neumann condition, and the above equations are equivalent to the following equation for both the compressible and incompressible formulations:

$$\mathbf{u} \cdot \mathbf{n} = 0, \qquad \mathbf{K} - (\mathbf{K} \cdot \mathbf{n})\mathbf{n} = \mathbf{0}$$
$$\mathbf{K} = \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T)\mathbf{n}$$

BOUNDARY SELECTION

For 2D axial symmetry, a boundary condition does not need to be defined for the symmetry axis at $r = 0$. The software automatically provides a condition that prescribes $u_r = 0$ and vanishing stresses in the z direction and adds an **Axial Symmetry** node that implements these conditions on the axial symmetry boundaries only.

CONSTRAINT SETTINGS

This section is displayed by clicking the **Show** button (⏿) and selecting **Advanced Physics Options**.

Open Boundary

The **Open Boundary** condition describes boundaries in contact with a large volume of fluid. Fluid can both enter and leave the domain on boundaries with this type of condition.

BOUNDARY CONDITIONS

The **Boundary condition** options for open boundaries are **Normal stress** and **No viscous stress**.

Normal Stress
The **Normal stress** f_0 condition implicitly imposes $p \approx f_0$.

When **Include gravity** is selected and **Use reduced pressure** not selected in the interface **Physical model** section, the **Compensate for hydrostatic pressure approximation** (named **Compensate for hydrostatic pressure** for incompressible flows) check box is available and selected by default. When it is selected, the hydrostatic pressure is automatically added to the pressure entered in f_0 user input.

No Viscous Stress

The **No Viscous Stress** condition specifies vanishing viscous stress on the boundary. This condition does not provide sufficient information to fully specify the flow at the open boundary and must at least be combined with pressure constraints at adjacent points.

The **No viscous stress** condition prescribes:

$$\left(\mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla\cdot\mathbf{u})\mathbf{I}\right)\mathbf{n} \ = \ \mathbf{0}$$

$$\mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T)\mathbf{n} \ = \ \mathbf{0}$$

for the compressible and the incompressible formulations. This condition can be useful in some situations because it does not impose any constraint on the pressure. A typical example is a model with volume forces that give rise to pressure gradients that are hard to prescribe in advance. To make the model numerically stable, this boundary condition should be combined with a point constraint on the pressure.

Boundary Stress

The **Boundary Stress** node adds a boundary condition that represents a general class of conditions also known as traction boundary conditions.

BOUNDARY CONDITION

The **Boundary condition** options for the boundary stress are **General stress**, **Normal stress**, and **Normal stress, normal flow**.

General Stress

When **General stress** is selected, the components for the **Stress F** should be specified. The total stress on the boundary is set equal to the given stress **F**:

$$\left(-p\mathbf{I} + \left(\mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla\cdot\mathbf{u})\mathbf{I}\right)\right)\mathbf{n} \ = \ \mathbf{F}$$

$$(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T))\mathbf{n} \ = \ \mathbf{F}$$

for the compressible and the incompressible formulations.

This boundary condition implicitly sets a constraint on the pressure that for 2D flows is

$$p = 2\mu\frac{\partial u_n}{\partial n} - \mathbf{n} \cdot \mathbf{F} \tag{6-1}$$

If $\partial u_n/\partial n$ is small, Equation 6-1 states that $p \approx -\mathbf{n} \cdot \mathbf{F}$.

Normal Stress
Normal Stress is described for the Open Boundary node.

Normal Stress, Normal Flow
For **Normal stress, normal flow**, the magnitude of the **Normal stress** f_0 should be specified. The tangential velocity is set to zero on the boundary:

$$\mathbf{n}^T\left(-p\mathbf{I} + \left(\mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right)\right)\mathbf{n} = -f_0, \qquad \mathbf{t} \cdot \mathbf{u} = 0$$

$$\mathbf{n}^T(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T))\mathbf{n} = -f_0, \qquad \mathbf{t} \cdot \mathbf{u} = 0$$

for the compressible and the incompressible formulations.

This boundary condition implicitly sets a constraint on the pressure that for 2D flows is

$$p = 2\mu\frac{\partial u_n}{\partial n} + f_0 \tag{6-2}$$

If $\partial u_n/\partial n$ is small, Equation 6-2 states that $p \approx f_0$.

When **Include gravity** is selected and **Use reduced pressure** not selected in the interface **Physical model** section, the **Compensate for hydrostatic pressure approximation** (named **Compensate for hydrostatic pressure** for incompressible flows) check box is available and selected by default. When it is selected, the hydrostatic pressure is automatically added to the pressure entered in f_0 or $p_{hydro}\mathbf{n}$ is added to $\mathbf{F}$ depending of the selected option.

CONSTRAINT SETTINGS

This section is displayed by clicking the **Show** button (👁) and selecting **Advanced Physics Options**.

If Normal Stress, Normal Flow is selected as the **Boundary condition**, then to **Apply reaction terms on** all dependent variables, the **All physics (symmetric)** option should be

selected. Alternatively, the **Individual dependent variables** could be selected to restrict the reaction terms as needed.

Periodic Flow Condition

The **Periodic Flow Condition** splits its selection into a source group and a destination group (the **Destination Selection** section is optional). Fluid that leaves the domain through one of the destination boundaries enters the domain through the corresponding source boundary. This corresponds to a situation where the geometry is a periodic part of a larger geometry. If the boundaries are not parallel to each other, the velocity vector is automatically transformed.

If the boundaries are curved, the orientation of the source must be specified manually (see Orientation of Source).

No input is required when **Compressible flow (Ma<0.3)** is selected for **Compressibility** under the **Physical Model** section for the physics interface. Typically when a periodic boundary condition is used with a compressible flow, the pressure is the same at both boundaries and the flow is driven by a volume force.

BOUNDARY SELECTION

The software usually automatically identifies the boundaries as either source boundaries or destination boundaries, as indicated in the selection list. This works fine for cases like opposing parallel boundaries. In other cases, right-click **Periodic Flow Condition** and select **Manual Destination Selection** to control the destination. By default it contains the selection that COMSOL Multiphysics identifies.

DESTINATION SELECTION
This section is available for specifying the destination boundaries, if needed, when the **Manual Destination Selection** option is selected in the context menu for the **Periodic Flow Condition** node. You can only select destination boundaries from the union of all source and destination boundaries.

FLOW CONDITION
This section is available when **Incompressible flow** is selected for **Compressibility** under the **Physical Model** section for the physics interface.

The **Flow Condition** at the boundary is specified through a value or expression for either the **Pressure difference**, $p_{src} - p_{dst}$, or the **Mass flow**, $\dot{m}$. The mass flow option ensures

a pressure difference is achieved across the source and destination boundaries. This pressure difference can, for example, drive the fully developed flow in a channel.

To set up a periodic boundary condition, both boundaries must be selected in the **Periodic Flow Condition** node. COMSOL Multiphysics automatically assigns one boundary as the source and the other as the destination. To manually set the destination selection, a **Destination Selection** subnode is available from the context menu (by right-clicking the parent node) or from the **Physics** toolbar, **Attributes** menu. All destination sides must be connected.

ORIENTATION OF SOURCE

To display this section, click the **Show More Options** button (👁) and select **Advanced Physics Options** in the **Show More Options** dialog box. For information about the **Orientation of Source** section, see Orientation of Source and Destination in the *COMSOL Multiphysics Reference Manual*.

ORIENTATION OF DESTINATION

This section appears if the setting for **Transform to intermediate map** in the **Orientation of Source** section is changed from the default value, **Automatic**, and **Advanced Physics Options** is selected in the **Show More Options** dialog box. For information about the **Orientation of Destination** section, see Orientation of Source and Destination in the *COMSOL Multiphysics Reference Manual*.

MAPPING BETWEEN SOURCE AND DESTINATION

To display this section, click the **Show More Options** button (👁) and select **Advanced Physics Options** in the **Show More Options** dialog box. For information about the **Mapping Between Source and Destination** section, see Mapping Between Source and Destination in the *COMSOL Multiphysics Reference Manual*.

Porous Interface

The **Porous Interface** condition is designed to properly account for a sudden jump in porosity, ε_p, across a boundary between different domains. It describes possible discontinuity of stress across the interface, and also reveals modified behavior of tangential velocity due to boundary layer on the upstream side of the interface. Choose among the following options under the **Continuity conditions**:

• **Velocity and stress** — stress continuity is invoked;

- **Velocity and porosity-corrected stress** (default)— the sum of stress and a contribution due to the inertial term being constant across the interface;

- **Velocity and porosity-corrected stress with loss** — the sum of the stress and a contribution due to the inertial term is lost in the downstream direction.

All three options give continuity of the velocity across the interface in constant-density flows, while in case of a jump in density:

1 give continuity of the mass flux (product of density and normal velocity) and tangential velocity;

2 account for the density-jump correction in the stress condition.

When **Velocity and porosity-corrected stress with loss** is chosen, a **Pressure loss model** needs to be specified. The options are:

- **User-defined loss coefficients** (default). Enter values for **Expansion loss coefficient** and **Contraction loss coefficient**;

- **Borda–Carnot**. Specify **Vena contracta model**.

Vena contracta model allows two options:

- **User defined** (default) — enter value of **Vena contracta coefficient**;

- **Weisbach** — enter values of **Lower limit** and **Exponent**.

Notice that the notions 'expansion' and 'contraction' used in this section correspond not to geometrical changes, but to the variations of the microscopic structure across the interface in the flow direction — increasing or decreasing porosity, ε_p, respectively.

Flow Continuity

The **Flow Continuity** condition is suitable for pairs where the boundaries match; it prescribes that the flow field is continuous across the pair.

The parts of the boundary where a source boundary lacks a corresponding destination boundary and vice versa will get conditions from other boundary conditions under the physics interface acting as fallback boundary conditions on the nonoverlapping parts. By default, the Wall node is used as fallback unless another feature has been selected for the boundary.

When the condition is set for pairs adjacent to domains with different porosity ε_p, it imposes conditions identical to the **Porous Interface** feature, which is designed to properly account for a sudden jump in porosity. See the section Porous Interface above

for further details (note that the **Flow Continuity** does not account for the density-jump corrections),

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| 🔍 | About Identity and Contact Pairs |

Pressure Point Constraint

The **Pressure Point Constraint** condition can be used to specify the pressure level. If it is not possible to specify the pressure level using a boundary condition, the pressure level must be set in some other way, for example, by specifying a fixed pressure at a point.

PRESSURE CONSTRAINT

The relative pressure value is set by specifying the **Pressure** p_0. If the reference pressure p_{ref} defined at the physics interface level is equal to zero, p_0 represents the absolute pressure.

When **Include gravity** is selected and **Use reduced pressure** not selected in the interface **Physical model** section, the **Compensate for hydrostatic pressure approximation** (named **Compensate for hydrostatic pressure** for incompressible flows) check box is available and selected by default. When it is selected, the hydrostatic pressure is automatically added to the pressure entered in p_0 user input.

CONSTRAINT SETTINGS

This section is displayed by clicking the **Show** button (👁) and selecting **Advanced Physics Options**.

The **Apply reaction terms on** setting is set per default to **Individual dependent variables**. **All physics (symmetric)** cannot be used together with a segregated solver when fluid flow is coupled with Moving Mesh, Level Set, or Phase Field in Fluids.

Point Mass Source

This feature requires at least one of the following licenses: Battery Design Module, CFD Module, Chemical Reaction Engineering Module, Corrosion Module, Electrochemistry Module, Electrodeposition Module, Fuel Cell & Electrolyzer Module, Microfluidics Module, Pipe Flow Module, or Subsurface Flow Module.

The **Point Mass Source** feature models mass flow originating from an infinitely small domain centered around a point.

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, there are two nodes: one for the fluid flow (**Fluid Point Source**) and one for the species (**Species Point Source**).

SOURCE STRENGTH

The source **Mass flux**, $\dot{q}_p$ should be specified. A positive value results in mass being ejected from the point into the computational domain. A negative value results in mass being 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 a point source located on a symmetry plane has twice the given strength.

⊕	Mass Sources for Fluid Flow in the *COMSOL Multiphysics Reference Manual*

Line Mass Source

This feature requires at least one of the following licenses: Battery Design Module, CFD Module, Chemical Reaction Engineering Module, Corrosion Module, Electrochemistry Module, Electrodeposition Module, Fuel Cell & Electrolyzer Module, Microfluidics Module, Pipe Flow Module, or Subsurface Flow Module.

The **Line Mass Source** feature models mass flow originating from a tube region with infinitely small radius.

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, there are two nodes, one for the fluid flow (**Fluid Line Source**) and one for the species (**Species Line Source**).

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 axis of symmetry
3D	Edges

SOURCE STRENGTH

The source **Mass flux**, $\dot{q}_l$, should be specified. A positive value results in mass being ejected from the line into the computational domain and a negative value means that mass is removed from the computational domain.

Line sources located on a boundary affect the adjacent computational domains. This, for example, has the effect that a line source located on a symmetry plane has twice the given strength.

Q	Mass Sources for Fluid Flow in the *COMSOL Multiphysics Reference Manual*

Gravity

The **Gravity** global feature is automatically added when **Include gravity** is selected at the interface level in the **Physical Model** settings. It defines the gravity forces from the **Acceleration of gravity** value.

ACCELERATION OF GRAVITY

The **Acceleration of gravity** (SI unit m/s, default value $-g_{const}\mathbf{e_z}$ in 2D axial symmetry and 3D and $-g_{const}\mathbf{e_y}$ in 2D) is used to define the gravity forces. It should be a global quantity.

The Darcy's Law Interface

The **Darcy's Law (dl)** interface ( ), found under the **Porous Media and Subsurface Flow** branch ( ) when adding a physics interface, is used to simulate fluid flow through interstices in a porous medium. It can be used to model low-velocity flows or media where the permeability and porosity are very small, and for which the pressure gradient is the major driving force and the flow is mostly influenced by the frictional resistance within the pores. Set up multiple **Darcy's Law** interfaces to model multiphase flows involving more than one mobile phase. The Darcy's Law interface can be used for stationary and time-dependent analyses.

The main feature is the **Porous Medium** Properties node, which provides interfaces for defining the fluid material and the porous matrix properties.

When this physics interface is added, the following default nodes are also added in the **Model Builder** — **Porous Medium**, **No Flow** (the default boundary condition), and **Initial Values**. Then, from the **Physics** toolbar, add other nodes that implement, for example, boundary conditions and mass sources. You can also right-click **Darcy's Law** 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 `dl`.

PHYSICAL MODEL

Enter a **Reference pressure level** p_{ref} (SI unit: Pa). The default value is `1[atm]`.

GRAVITY EFFECTS

By default there are no gravity effects added to Darcy's Law interface. Select the check box **Include gravity** to activate the acceleration of gravity. When this check box is selected, a global **Gravity** feature node is shown in the interface model tree.

Enter a value for the acceleration of gravity. The default value `g_const` is the predefined standard acceleration of gravity on earth.

	For a detailed overview of the functionality available in each product, visit https://www.comsol.com/products/specifications/.

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.

You can choose the order of the shape functions used for the pressure variable solved by the Darcy's Law interface. The default shape functions are **Quadratic** Lagrange.

The **Compute boundary fluxes** check box is not activated by default. When this option is selected, 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.

Also, the **Apply smoothing to boundary fluxes** check box is available if the previous check box is checked. The smoothing can provide a better 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 transport 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*.

The dependent variable (field variable) is the **Pressure**. The name can be changed but the names of fields and dependent variables must be unique within a model.

🔍	• Domain, Boundary, Edge, Point, and Pair Nodes for the Darcy's Law Interface • Theory for the Darcy's Law Interface • Physical Constants in the *COMSOL Multiphysics Reference Manual*

▥	• *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** • *Steam Reformer*: Application Library path **Chemical_Reaction_Engineering_Module/Reactors_with_Porous_Catalysts/steam_reformer** • *Terzaghi Compaction*: Application Library path **Subsurface_Flow_Module/Poromechanics/terzaghi_compaction**

Domain, Boundary, Edge, Point, and Pair Nodes for the Darcy's Law Interface

The Darcy's Law Interface has the following domain, boundary, edge, point, and pair nodes, these 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).

DOMAIN

- Porous Medium
- Unsaturated Porous Medium
- Dual Porosity Medium
- Dual Permeability Medium
- Unsaturated Dual Permeability Medium

- Mass Source
- Cross Section
- Initial Values
- Unsaturated Porous Medium
- ThicknessContributing Velocity
- Porous Electrode Coupling

BOUNDARY, EDGE, AND POINT

The following nodes (listed in alphabetical order) are available on exterior boundaries:

- Atmosphere/Gauge
- Electrode Surface Coupling
- Flux Discontinuity
- Fracture
- Hydraulic Head
- Inlet
- Interior Wall
- Line Mass Source
- Mass Flux
- No Flow

- Outlet
- Pervious Layer
- Point Mass Source
- Precipitation
- Pressure
- Pressure Head
- Reaction Coefficients[1]
- Symmetry
- Thin Barrier

[1] This node is described for the Transport of Diluted Species Interface

The relevant physics interface condition at interior boundaries is continuity:

$$\mathbf{n} \cdot (\rho_1 \mathbf{u}_1 - \rho_2 \mathbf{u}_2) = 0$$

The continuity boundary condition ensures that the pressure and mass flux are continuous. In addition, the Pressure boundary condition is available on interior boundaries.

The continuity boundary condition provides continuity for the pressure and mass flux. In addition, the following boundary conditions are available on interior boundaries:

- Pressure
- Pressure Head
- Hydraulic Head
- Interior Wall

- Pervious Layer
- Flux Discontinuity
- Fracture
- Thin Barrier

🔍 Note that some of the above-mentioned domain or boundary conditions are only available with some products. For a detailed overview of the functionality available in each product, visit https://www.comsol.com/products/specifications/

💡 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.

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 the axial symmetry boundaries only.

❗ 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.

Porous Medium

The **Porous Medium** node adds the equations for modeling flow through porous domains. By default these are Equation 6-3 and Equation 6-4 (excluding any mass sources).

$$\frac{\partial}{\partial t}(\varepsilon_p \rho) + \nabla \cdot (\rho \mathbf{u}) = Q_m \tag{6-3}$$

$$\mathbf{u} = -\frac{\kappa}{\mu}\nabla p \qquad\qquad (6\text{-}4)$$

For a steady-state problem the first term in Equation 6-3 disappears. When Mass Source is active Equation 6-4 is of the following form:

$$\mathbf{u} = -\frac{\kappa}{\mu}(\nabla p - \rho\mathbf{g}) \qquad\qquad (6\text{-}5)$$

The **Porous Medium** feature has two default subfeatures — the Fluid subfeature where the fluid density ρ (SI unit: kg/m^3) and dynamic viscosity μ (SI unit: Pa·s) are defined and the Porous Matrix subfeature where the permeability κ (SI unit: m^2) and porosity ε_p (dimensionless) are specified.

COORDINATE SYSTEM SELECTION

Select a coordinate system from the **Coordinate system** list for the interpretation of directions in anisotropic material properties. The default is the **Global coordinate system**, and the list contains any additional orthonormal coordinate system (except boundary coordinate systems) added under the **Definitions** node.

The subnodes inherit these coordinate system settings. In particular, the **Permeability** or **Hydraulic conductivity** (in the Porous Matrix subnode) should be set according to the coordinate system selected in this section.

FLOW MODEL

Define if the flow follows a linear or nonlinear pressure-velocity relationship.

- **Darcian flow** (default) defines a linear relationship using Equation 6-3 and Equation 6-4.

- **Non-Darcian flow** defines a nonlinear relationship using Equation 6-3 and

$$\nabla p = -\frac{\mu}{\kappa}\mathbf{u} - \beta\rho|\mathbf{u}|\mathbf{u}$$

    where the nonlinear parameter β (SI unit: $1/m$) is further specified in the Porous Matrix subfeature.

STORAGE MODEL

Define the time dependent storage term by selecting one of the following options from the drop-down menu:

- **From density and porosity** (default), uses the formulation of Equation 6-3

- **Linearized storage**, where the following linear equation is used to define the storage:

$$S_p = \varepsilon_p \chi_f + (1 - \varepsilon_p) \chi_p$$

- **Poroelastic storage**, where $S_p = \varepsilon_p \chi_f$
- **Quasistatic**, where the storage term is set to zero
- **User defined** to directly specify the storage coefficient S_p

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🔍
- Porous Material in the *COMSOL Multiphysics Reference Manual*
- About Darcian and Non-Darcian Flow in the *Porous Media Flow Module User's Guide*
- Storage Models in the *Subsurface Flow Module User's Guide*

🔍 Note that some options are only available in some modules. For a detailed overview of the functionality available in each product, visit https://www.comsol.com/products/specifications/

Fluid

This node defines the material properties of the fluid of the Porous Medium, the Unsaturated Porous Medium, the Dual Porosity Medium, the Dual Permeability Medium, or the Unsaturated Porous Medium parent node.

MODEL INPUT

This section contains fields and values that are inputs for expressions defining material properties. If such user-defined property groups are added, the model inputs appear here.

FLUID PROPERTIES

The available options for the **Fluid type** are **Incompressible**, **Compressible**, **Compressible, linearized**, or **Ideal gas**. The selection determines how the density and compressibility of the fluid are set.

Incompressible
The default **Reference density** ρ_{ref} uses values **From material**. For **User defined** enter another value or expression.

Compressible

The default **Density** ρ uses values **From material**. For **User defined** enter another value or expression as a function of the absolute pressure. The compressibility of the fluid is computed from it.

Compressible, Linearized

The default **Reference density** ρ_{ref} and the **Fluid compressibility** χ_f use values **From material**. For **User defined** enter another value or expression. The fluid density increases linearly as a function of the fluid pressure.

Ideal Gas

For **Ideal gas** it uses the ideal gas law to describe the gas density. In this case, specify the thermodynamics properties. Select a **Gas constant type** — **Specific gas constant** R_s (the default) or **Mean molar mass** M_n (SI unit: J/(mol·K)). For **Mean molar mass** the universal gas constant $R = 8.314$ J/(mol·K) is used as the built-in physical constant. For both properties, the defaults use values **From material**. For **User defined** enter another value or expression.

For all fluid types specify the **Dynamic viscosity** μ (SI unit: Pa·s) uses values **From material**. For **User defined** enter another value or expression.

Porous Matrix

This node defines the porosity and material properties of the solid matrix of the Porous Medium or Unsaturated Porous Medium parent node.

MODEL INPUT

This section contains fields and values that are inputs for expressions defining material properties. If such user-defined property groups are added, the model inputs appear here.

MATRIX PROPERTIES

The default **Porosity** ε_p of the solid matrix is taken **From material**. In a **Porous Material** node, the porosity is defined as follows:

$$\varepsilon_p = 1 - \sum_i \theta_{si} - \sum_i \theta_{imfi}$$

where θ_{si} and θ_{imfi} are the porosities of the **Solid** and **Immobile Fluids** subnodes under the **Porous Material** node. See Porous Material in the *COMSOL Multiphysics Reference Manual* for more information.

Select **User defined** to enter a value or expression for ε_p.

If required by a **Storage model** in the parent node, specify the **Effective compressibility** of the porous matrix. The default value is $\chi_p = 10^{-4}$ 1/Pa.

Select a **Permeability model** to specify the capacity of the porous material to transmit flow. Which options are available depends on the **Flow model** setting in the parent node. Note that for the Unsaturated Porous Medium parent node only the Darcian Flow models are available.

Darcian Flow

If **Darcian flow** is selected in the parent **Porous medium** node, select between the following options for the **Permeability model**:

- Select **Permeability** (default) to define the permeability of the porous matrix. The default **Permeability** κ (SI unit: m^2) uses the value **From material**, as defined by the **Porous material**. For **User defined** select **Isotropic** to define a scalar value or **Diagonal** or **Symmetric** to define a tensor value.

- Select **Hydraulic conductivity** or define a combination of fluid permeability and dynamic viscosity. For **Hydraulic conductivity** K (SI unit: m/s) select **Isotropic** to define a scalar value or **Diagonal** or **Symmetric** to define a tensor value. The default is $2.94 \cdot 10^{-4}$ m/s.

- Select **Kozeny-Carman** to define the permeability from the porosity and mean particle diameter. Enter the mean **Particle diameter** d_p (SI unit: m), the default value is 0.5 mm.

Non-Darcian Flow

If **Non-Darcian flow** is selected in the parent node, select between the following options for the **Permeability model**:

- For **Forchheimer**, the default **Permeability** κ (SI unit: m^2) uses the value **From material**. Furthermore, the dimensionless **Forchheimer parameter** c_F can be defined. The default value is 0.55.

- If **Ergun** is selected, enter the mean **Particle diameter** d_p (default value: 0.5 mm).

- For **Burke–Plummer**, specify the mean **Particle diameter** d_p (default value: 0.5 mm).
- For **Klinkenberg**, the default **Permeability** κ_∞ (SI unit: m^2) uses the value **From material**. Enter the **Klinkenberg parameter** b_K. Its default value is 10^3 Pa.

🔍	• About Darcian and Non-Darcian Flow in the *Porous Media Flow Module User's Guide* • Permeability Models in the *Porous Media Flow Module User's Guide*

🔍	Note that some options are only available in some modules. For a detailed overview of the functionality available in each product, visit https://www.comsol.com/products/specifications/

RETENTION MODEL

For an Unsaturated Porous Medium select between the following options for the retention model:

- **van Genuchten**, to specify the retention model using the van Genuchten relationship. Enter the constitutive relation constants α (the default value is 1, and the SI unit is 1/m), n (default value is 2), and l (default value is 0.5). The constitutive parameter m is equal to $1 - 1/n$.
- **Brooks and Corey** to use the retention model according to the Brooks and Corey relationships.
- **User defined** to use a different retention model. Enter user defined expressions for the **Effective saturation** S_e, the **Liquid volume fraction** θ_l. The default is ε_p (the porosity variable). Specify the **Specific moisture capacity** C_m (SI unit: 1/m). The default value is 0 (1/m). Enter an expression for the **Relative permeability** κ_r. The default value is 1.

If there is a residual volume of liquid that cannot move through the pore network, also enter a value between 0 and 1 for the **Residual liquid volume fraction** θ_r. The default value is 0.

🔍	Retention and Permeability Relationships in the *Subsurface Flow Module User's Guide*

Unsaturated Porous Medium

The **Unsaturated Porous Medium** node adds the Richards' equation (Equation 6-6) for flow in variably saturated porous media.

$$\rho\left(\frac{C_m}{\rho g} + S_e S_p\right)\frac{\partial p}{\partial t} + \nabla \cdot \rho\left(-\frac{\kappa_r \kappa}{\mu}(\nabla p + \rho g \nabla D)\right) = Q_m \tag{6-6}$$

The Unsaturated Porous Medium feature has two default subfeatures: the Fluid subfeature, where the fluid density ρ (SI unit: kg/m^3) and viscosity μ (SI unit: Pa·s) are defined, and the Porous Matrix subfeature, where the permeability κ (SI unit: m^2) and porosity ε_p (dimensionless) are specified as well as the retention model.

COORDINATE SYSTEM SELECTION

Select a coordinate system from the **Coordinate system** list for the interpretation of directions in anisotropic material properties. The default is the **Global coordinate system**, and the list contains any additional orthonormal coordinate system (except boundary coordinate systems) added under the **Definitions** node.

The subnodes inherit these coordinate system settings. In particular, the **Permeability** or **Hydraulic conductivity** (in the Porous Matrix subnode) should be set according to the coordinate system selected in this section.

STORAGE MODEL

With this option, define the first term in Equation 6-6. Therefore, choose from a drop-down menu one of the following formulations:

- From retention model
- Linearized storage (default)
- From liquid content
- User defined

If **From retention model** is chosen, the first term of Equation 6-6 accounts only for the specific moisture capacity C_m which is defined by the Retention Model in the Porous Matrix subnode:

$$\frac{C_m}{g}\frac{\partial p}{\partial t} \ .$$

For the option **Linearized storage** the storage coefficient S_p in Equation 6-6 is defined as

$$S_{\mathrm{p}} = \varepsilon_{\mathrm{p}}\chi_{\mathrm{f}} + (1 - \varepsilon_{\mathrm{p}})\chi_{\mathrm{p}}.$$

From liquid content enforces the first term of Equation 6-6 to be defined in terms of liquid volume fraction as

$$\frac{\partial(\rho\theta_{\mathrm{l}})}{\partial t}$$

and the **User defined** option allows to define the storage coefficient S_{p} in Equation 6-6 directly.

> 🔍 Note that some options are only available in some modules. For a detailed overview of the functionality available in each product, visit https://www.comsol.com/products/specifications/

Dual Porosity Medium

Use the Dual Porosity Medium if the flow through macropores is governed by Darcy's law and the micropores do not significantly contribute to the overall flow in the porous medium.

The feature has three default subfeatures —the Fluid subfeature where the fluid density ρ (SI unit: kg/m^3) and dynamic viscosity μ (SI unit: Pa·s) are defined, the Macropores subfeature where the hydraulic properties of the macroporous matrix are defined, and the Micropores where the hydraulic properties of the microporous matrix are defined.

COORDINATE SYSTEM SELECTION

Select a coordinate system from the **Coordinate system** list for the interpretation of directions in anisotropic material properties. The default is the **Global coordinate system**, and the list contains any additional orthonormal coordinate system (except boundary coordinate systems) added under the **Definitions** node.

The subnodes inherit these coordinate system settings. In particular, the **Permeability** or **Hydraulic conductivity** (in the Macropores and Micropores subnodes) should be set according to the coordinate system selected in this section.

STORAGE MODEL

Choose from a drop-down menu one of the following formulations:

- **From density and porosity** (default), uses the formulation equivalent to Equation 6-3

- **Linearized storage**, where the following linear equation is used to define the storage in the macropores as $S_p = \varepsilon_p \chi_f + (1 - \varepsilon_p)\chi_p$ and in the micropores as $S_{p,m} = \varepsilon_{p,m} \chi_f + (1 - \varepsilon_{p,m})\chi_p$.

- **Poroelastic storage**, where $S_p = \varepsilon_p \chi_f$ in the macropores and $S_{p,m} = \varepsilon_{p,m} \chi_f$ in the micropores.

- **Quasistatic**, where the storage term is set to zero

- **User defined** to directly specify the storage coefficient S_p and $S_{p,m}$ for the macro- and micropores respectively.

⊚	• Storage Models in the *Subsurface Flow Module User's Guide*

INTERPOROSITY FLOW

Specify the **Fluid Transfer Function** α_w which is used to calculate the interporosity flow, the mass exchange between macro- and microscale system:

$$Q_{ip} = \alpha_w(p_M - p_m) \tag{6-7}$$

with p_M being the pressure within the macropores and p_m the pressure within the micropores.

⊚	Find more information in the *Subsurface Flow Module User's Guide* • Dual Porosity & Dual Permeability Modeling • Dual Porosity and Dual Permeability Theory

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⊚	Note that some options are only available in some modules. For a detailed overview of the functionality available in each product, visit https://www.comsol.com/products/specifications/

Dual Permeability Medium

Use the **Dual Permeability Medium** feature to model transport in a saturated dual permeability medium where Darcy's Law describes the transport in each system.

The feature has three default subfeatures —the Fluid subfeature where the fluid density ρ (SI unit: kg/m^3) and dynamic viscosity μ (SI unit: Pa·s) are defined, the Macropores

subfeature where the hydraulic properties of the macroporous matrix are defined, and the Micropores where the hydraulic properties of the microporous matrix are defined.

COORDINATE SYSTEM SELECTION

Select a coordinate system from the **Coordinate system** list for the interpretation of directions in anisotropic material properties. The default is the **Global coordinate system**, and the list contains any additional orthonormal coordinate system (except boundary coordinate systems) added under the **Definitions** node.

The subnodes inherit these coordinate system settings. In particular, the **Permeability** or **Hydraulic conductivity** (in the Macropores and Micropores subnodes) should be set according to the coordinate system selected in this section.

STORAGE MODEL

With this option under the **Porous Medium** section, Equation 6-3 is formulated with respect to a storage term (analogous to Equation 4-4). Therefore, choose from a drop-down menu one of the following formulations:

- **From density and porosity** (default), uses the formulation of Equation 4-4
- **Linearized storage**, where the following linear equation is used to define the storage:

$$S_{p,i} = \varepsilon_{p,i}\chi_f + (1 - \varepsilon_{p,i})\chi_{p,i}$$

with $i=M$ for the macropores and $i=m$ for the micropores.

- **Poroelastic storage**, where $S_{p,i} = \varepsilon_{p,i}\chi_f$
- **Quasistatic**, where the storage term is set to zero
- **User defined** to directly specify the storage coefficient S_p

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🔍   • Storage Models in the *Subsurface Flow Module User's Guide*

INTERPOROSITY FLOW

Specify the **Fluid Transfer Function** α_w which is used to calculate the interporosity flow, which is the mass exchange between macro- and microscale system:

$$Q_{ip} = \alpha_w(p_M - p_m) \tag{6-8}$$

with p_M being the pressure in the macropores and p_m the pressure in the micropores.

🔍	Find more information in the *Subsurface Flow Module User's Guide* • Dual Porosity & Dual Permeability Modeling • Dual Porosity and Dual Permeability Theory

🔍	Note that some options are only available in some modules. For a detailed overview of the functionality available in each product, visit https://www.comsol.com/products/specifications/

Unsaturated Dual Permeability Medium

Use the **Unsaturated Dual Permeability Medium** feature to model the transport in an unsaturated dual permeability medium where the Richards' Equation (Equation 6-6) describes the transport in each system.

$$\theta_M \left(\rho \left(S_{e,M} S_{p,M} + \frac{C_{m,M}}{\rho g} \right) \frac{\partial p_M}{\partial t} + \nabla(\rho \mathbf{u}_M) \right) = -Q_{ip} + \theta_M Q_m$$

$$(1 - \theta_M) \left(\rho \left(S_{e,m} S_{p,m} + \frac{C_{m,m}}{\rho g} \right) \frac{\partial p_m}{\partial t} + \nabla(\rho \mathbf{u}_m) \right) = Q_{ip} + (1 - \theta_M) Q_m \qquad (6\text{-}9)$$

$$p = \theta_M p_M + (1 - \theta_M) p_m$$

θ_M is the volume fraction of the macropores, Q_{ip} is the interporosity flow which is the mass transfer from the macroscale to the microscale system. The indices M and m stand for macropores and micropores, respectively.

The feature has three default subfeatures —the Fluid subfeature where the fluid density ρ (SI unit: kg/m^3) and dynamic viscosity μ (SI unit: Pa·s) are defined, the Macropores subfeature where the hydraulic properties of the macroporous matrix are defined, and the Micropores where the hydraulic properties of the microporous matrix are defined.

COORDINATE SYSTEM SELECTION

Select a coordinate system from the **Coordinate system** list for the interpretation of directions in anisotropic material properties. The default is the **Global coordinate system**, and the list contains any additional orthonormal coordinate system (except boundary coordinate systems) added under the **Definitions** node.

The subnodes inherit these coordinate system settings. In particular, the **Permeability** or **Hydraulic conductivity** (in the Macropores and Micropores subnodes) should be set according to the coordinate system selected in this section.

STORAGE MODEL

With this option, define the first term in Equation 6-9. Therefore, choose from a drop-down menu one of the following formulations:

- From retention model
- Linearized storage (default)
- From liquid content
- User defined

If **From retention model** is chosen, the first term of Equation 6-9 accounts only for the specific moisture capacity $C_{m,i}$ which is defined by the Retention Model in the Macropores (i=M) or Micropores (i=m) subnode:

$$\frac{C_{mi}}{g}\frac{\partial p}{\partial t}\,.$$

For the option **Linearized storage** the storage coefficient $S_{p,i}$ in Equation 6-9 is defined as

$$S_{p,i} \,=\, \varepsilon_{p,i}\chi_f + (1-\varepsilon_{p,i})\chi_{p,i}\,.$$

From liquid content enforces the first term of Equation 6-9 to be defined in terms of liquid volume fraction as

$$\frac{\partial(\rho\theta_{l,i})}{\partial t}$$

- and the **User defined** option allows to define the storage coefficient $S_{p,i}$ in Equation 6-9 directly.

🔍 | • Storage Models in the *Subsurface Flow Module User's Guide*

INTERPOROSITY FLOW

Specify the **Fluid Transfer Function** α_w which is used to calculate the interporosity flow, which is the mass exchange between macro- and microscale system:

$$Q_{ip} = \alpha_w(p_M - p_m) \tag{6-10}$$

with p_M being the pressure within the macroscale system and p_m the pressure within the microscale system.

Q | • Dual Porosity & Dual Permeability Modeling in the *Subsurface Flow Module User's Guide*

Macropores

This node defines the porosity and material properties of the macroporous matrix of the Dual Porosity Medium, the Dual Permeability Medium, or the Unsaturated Dual Permeability Medium parent node.

MODEL INPUT

This section contains fields and values that are inputs for expressions defining material properties. If such user-defined property groups are added, the model inputs appear here.

VOLUME FRACTION

Here enter the **Volume Fraction of Macropores**, θ_M.

MATRIX PROPERTIES

The default **Porosity** $\varepsilon_{p,M}$ of the solid matrix of the macropore system is taken **From material**. Select **User defined** to enter a value or expression for $\varepsilon_{p,M}$.

If required by a **Storage model** in the parent node, specify the **Effective compressibility** of the porous matrix of the macropore system. The default value is $\chi_{p,M} = 10^{-4} \ 1/\text{Pa}$.

Select a **Permeability model** to specify the capacity of the porous material to transmit flow. For the macropore settings only the Darcian Flow models are available. Select between the following options for the **Permeability model**:

- Select **Permeability** (default) to define the permeability of the porous matrix. The default **Permeability** κ_M (SI unit: m^2) uses the value **From material**, as defined by the **Porous material**. For **User defined** select **Isotropic** to define a scalar value or **Diagonal** or **Symmetric** to define a tensor value.

- Select **Hydraulic conductivity** or define a combination of fluid permeability and dynamic viscosity. For **Hydraulic conductivity** K_M (SI unit: m/s) select **Isotropic** to

define a scalar value or **Diagonal** or **Symmetric** to define a tensor value. The default is $2.94 \cdot 10^{-4}$ m/s.

- Select **Kozeny-Carman** to define the permeability from the porosity and mean particle diameter. Enter the mean **Particle diameter** $d_{p,M}$ (SI unit: m), the default value is 0.5 mm.

RETENTION MODEL

For an Unsaturated Dual Permeability Medium select between the following options for the retention model:

- **van Genuchten**, to specify the retention model using the van Genuchten relationship. Enter the constitutive relation constants α (the default value is 1, and the SI unit is $1/m$), n (default value is 2), and l (default value is 0.5). The constitutive parameter m is equal to $1 - 1/n$.

- **Brooks and Corey** to use the retention model according to the Brooks and Corey relationships.

- **User defined** to use a different retention model. Enter user defined expressions for the **Effective saturation** $S_{e,M}$, the **Liquid volume fraction** $\theta_{l,M}$. The default is $\varepsilon_{p,M}$ (the porosity variable). Specify the **Specific moisture capacity** $C_{m,M}$ (SI unit: $1/m$). The default value is 0 ($1/m$). Enter an expression for the **Relative permeability** $\kappa_{r,M}$. The default value is 1.

If there is a residual volume of liquid that cannot move through the pore network, also enter a value between 0 and 1 for the **Residual liquid volume fraction** θ_r. The default value is 0.

⊙	Retention and Permeability Relationships in the *Subsurface Flow Module User's Guide*

Micropores

This node defines the porosity and material properties of the microporous matrix of the Dual Porosity Medium, Dual Permeability Medium, or the Unsaturated Dual Permeability Medium parent node.

MODEL INPUT

This section is only available for the Unsaturated Dual Permeability Medium parent node and contains fields and values that are inputs for expressions defining material

properties. If such user-defined property groups are added, the model inputs appear here.

MATRIX PROPERTIES

The default **Porosity** $\varepsilon_{p,m}$ of the solid matrix of the micropore system is taken **From material**. Select **User defined** to enter a value or expression for $\varepsilon_{p,m}$.

If required by a **Storage model** in the parent node, specify the **Effective compressibility** of the microscale porous matrix. The default value is $\chi_{p,m} = 10^{-4}$ 1/Pa.

Select a **Permeability model** to specify the capacity to transmit flow for the porous material of the microscale system. Here, only the Darcian Flow models are available. Select between the following options for the **Permeability model**:

- Select **Permeability** (default) to define the permeability of the porous matrix. The default **Permeability** κ_m (SI unit: m^2) uses the value **From material**, as defined by the **Porous material**. For **User defined** select **Isotropic** to define a scalar value or **Diagonal** or **Symmetric** to define a tensor value.

- Select **Hydraulic conductivity** or define a combination of fluid permeability and dynamic viscosity. For **Hydraulic conductivity** K_m (SI unit: m/s) select **Isotropic** to define a scalar value or **Diagonal** or **Symmetric** to define a tensor value. The default is $2.94 \cdot 10^{-4}$ m/s.

- Select **Kozeny-Carman** to define the permeability from the porosity and mean particle diameter. Enter the mean **Particle diameter** $d_{p,m}$ (SI unit: m), the default value is 0.5 mm.

RETENTION MODEL

For an Unsaturated Dual Permeability Medium select between the following options for the retention model:

- **From macropores** to take over the retention model settings from the **Macropores** node.

- **van Genuchten**, to specify the retention model using the van Genuchten relationship. Enter the constitutive relation constants α (the default value is 1, and the SI unit is 1/m), n (default value is 2), and l (default value is 0.5). The constitutive parameter m is equal to $1 - 1/n$.

- **Brooks and Corey** to use the retention model according to the Brooks and Corey relationships.

- **User defined** to use a different retention model. Enter user defined expressions for the **Effective saturation** $S_{e,m}$, the **Liquid volume fraction** $\theta_{l,m}$. The default is $\varepsilon_{p,m}$ (the

porosity variable). Specify the **Specific moisture capacity** $C_{m,m}$ (SI unit: $1/m$). The default value is 0 $(1/m)$. Enter an expression for the **Relative permeability** $\kappa_{r,m}$. The default value is 1.

If there is a residual volume of liquid that cannot move through the pore network, also enter a value between 0 and 1 for the **Residual liquid volume fraction** θ_r. The default value is 0.

🔍	Retention and Permeability Relationships in the *Subsurface Flow Module User's Guide*

INITIAL VALUES

Define the initial pressure of the microscale system. The default is to use the initial values defined in the Initial Values feature node which means that the same initial values apply to the macroscale and the microscale system.

Select **User Defined** to specify an initial pressure for the microscale system $p_{m0,init}$.

🔍	Note that some options are only available in some modules. For a detailed overview of the functionality available in each product, visit https://www.comsol.com/products/specifications/

Mass Source

The **Mass Source** node adds a mass source Q_m, which appears on the right-hand side of the Darcy's Law equation (Equation 6-3).

$$\frac{\partial}{\partial t}(\rho\varepsilon) + \nabla \cdot (\rho\mathbf{u}) = Q_m \qquad (6\text{-}11)$$

For the Fracture Flow interface, the mass source is applicable to the right-hand side of Equation 4-40 in the *Subsurface Flow Module User's Guide* (where it is multiplied with the fracture thickness).

MASS SOURCE

Enter a value or expression for the **Mass source** Q_m (SI unit: $kg/(m^3 \cdot s)$). The default is 0 $kg/(m^3 \cdot s)$.

Contributing Velocity

The **Contributing Velocity** node adds a velocity contribution $\mathbf{u}_{ctrb}$ to the velocity field $\mathbf{u}_d$ that is computed from the flow model selected in the parent Porous Medium, Unsaturated Porous Medium, or Dual Porosity Medium feature. The total velocity field used in the continuity equation is therefore

$$\mathbf{u} = \mathbf{u}_d + \mathbf{u}_{ctrb} \tag{6-12}$$

Such velocity contributions can arise in multiphysics models that involve, for example, transport of solutes. If several **Contributing Velocity** nodes are added under the same parent feature, the contributions are treated additively. The sum of all contributing velocity fields is available in the variables `name.Uctrb` (material frame) and `name.uctrb` (spatial frame), with `name` being the **Name** of the physics interface (for example, `dl`).

COORDINATE SYSTEM SELECTION

Select a coordinate system from the **Coordinate system** list to specify the coordinate system in which the contributing velocity field is given. The default is the **Global coordinate system**. Note that the coordinate system used to specify the components of the contributing velocity field can be selected independently of the coordinate system of the parent feature.

CONTRIBUTING VELOCITY

The default contributing velocity field $\mathbf{u}_{ctrb}$ is **User defined**, which lets you enter the components of the contributing velocity field explicitly. If a matching velocity field is announced by another feature, it will be available in the selection list.

ADVANCED

Select the **Frame** in which the contributing velocity field is specified. The default is the **Reference configuration**, which means that the velocity field follows the material under, for example, a rotation of the domain. If instead your contributing velocity field follows a fixed direction in space, select the **Deformed configuration**. This section is only displayed if **Advanced Physics Options** is activated and the spatial and material frame of the component differ, such as in the presence of a **Moving Mesh** or **Solid Mechanics** interface.

Initial Values

The **Initial Values** node adds an initial value for the pressure that can serve as an initial condition for a transient simulation or as an initial guess for a nonlinear solver.

If you have the Subsurface Flow Module licensed, you can specify the pressure either directly or as an expression for the pressure head, H_p, or the hydraulic head, H; the hydraulic head and the pressure head relate to the pressure p as

$$H_p = \frac{p}{\rho g}; \quad H = H_p + D$$

where ρ is the fluid density (SI unit: kg/m^3); g denotes the acceleration of gravity (SI unit: m/s^2); and D is the elevation (SI unit: m).

INITIAL VALUES

Enter a value or expression for the initial value of the **Pressure** p (SI unit: Pa). The default value is 0 Pa.

In case the Subsurface Flow Module is available, click the **Pressure head** button to enter a value or expression for H_p (SI unit: m). The default is 0 m. Click the **Hydraulic head** button to enter a value or expression for H (SI unit: m). The default is 0 m.

Gravity

The **Gravity** node is automatically added when **Include gravity** is selected at interface level in the **Darcy's Law** settings and it is active in all domains in which the Darcy's Law interface is applied.

COORDINATE SYSTEM SELECTION

The **Global coordinate system** is selected by default. The **Coordinate system** list contains any additional coordinate systems that the model includes. It can be used when prescribing the direction of the gravitational forces.

GRAVITY

Specify either the acceleration vector or — in case you have a Subsurface Flow Module license — the elevation.

When **Acceleration** is selected from the list, enter the components of the **Gravity vector g**. The default value is g_const which is the physical constant having the value 9.8066 m/s^2.

- For 3D and 2D axisymmetric models, the default value is -g_const in the z direction.
- For 2D models, the default value is -g_const in the y direction.

When **Elevation** is selected from the list, specify the **Elevation** D (SI unit: m). The **Acceleration of gravity** is taken **From physics interface** by default but could be overridden when **User defined** is selected.

When the check box **Include gravity** is not selected in the Darcy's Law interface Settings, the elevation D is set equal to zero.

Select the check box **Specify reference position** to define a reference position for the gravity calculation.

Cross Section

Use this node with 1D components to model domains with another cross-sectional area than the global one that is used in the interface **Physical Model** section. In 1D geometries, the pressure is assumed to be constant in the radial direction, and Darcy's Law accounts for that.

CROSS SECTION

Enter values for the **Cross-sectional area** A_c to set the cross section of the domain in the plane perpendicular to the 1D geometry.

Thickness

Use this node with 2D and 1D axisymmetric components to model domains with another thickness than the overall thickness that is specified in the interface **Physical Model** section. In 2D geometries, the pressure is assumed to be constant in the out-of-plane direction (the z direction with default spatial coordinate names). In 1D axisymmetric geometries the thickness represents the z direction.

THICKNESS

Specify a value for the **Thickness** d_z of the domain in the out-of-plane direction. This value replaces the overall thickness in the domains that are selected in the **Domain Selection** section, and is used to multiply some terms into the heat equation.

Porous Electrode Coupling

Use the **Porous Electrode Coupling** node to define a mass source based on the volumetric current densities of one or multiple **Porous Electrode Reaction** nodes in an Electrochemistry interface.

The source (or sink) is proportional to the **Molar mass (kg/mol)** of the reacting species, the current densities and the stoichiometric coefficients according to Faraday's law as defined by summation over the Reaction Coefficient subnodes.

SPECIES

Based on the number of species required for the model, use the **Add** (+) and **Delete** ≣) buttons under the table to add or remove **Species**. Then enter a value for the **Molar mass (kg/mol)** in the applicable rows for each species.

The setting in the table will determine the number of available fields for entering the stoichiometric coefficients of the Reaction Coefficient subnodes.

Electrode Surface Coupling

Use the **Electrode Surface Coupling** node to define a combined wall and inflow/outflow boundary condition based on current densities of one or multiple Electrode Reaction nodes in an Electrochemistry interface.

The flow is proportional to the **Molar mass (kg/mol)** of the reacting species, the current densities and the stoichiometric coefficients according to Faraday's law as defined by summation over the Reaction Coefficient subnodes.

SPECIES

Based on the number of species required for the model, use the **Add** (+) and **Delete** ≣) buttons under the table to add or remove **Species**. Then enter a value for the **Molar mass (kg/mol)** in the applicable rows for each species.

The setting in the table will determine the number of available field for entering the stoichiometric coefficients of the Reaction Coefficient subnodes.

Pressure

Use the **Pressure** node to specify the pressure on a boundary. In many cases the distribution of pressure is known, giving a Dirichlet condition $p = p_0$ where p_0 is a

known pressure given as a number, a distribution, or an expression involving time, t, for example.

PRESSURE

Enter a value or expression for the **Pressure** p_0 (SI unit: Pa). Enter a relative pressure value in p_0 (SI unit: Pa).

For the Subsurface Flow Module, the **Pressure** node provides the pressure P_0 as a condition on edges in 3D models. Then select the edges under **Edge Selection**.

CONSTRAINT SETTINGS

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

As an attribute to the Fracture boundary condition or as boundary condition to The Fracture Flow Interface (which are available in the Subsurface Flow Module and the Porous Media Flow Module), the pressure can also be specified on edges (in 3D) or points (in 2D) surrounding the fracture domain. In other cases, pressure constraints on edges or points are not implemented.

> ! If the boundary condition is adjacent to an Unsaturated Dual Permeability Medium feature it constrains the pressures in the Macropores and Micropores to p_0.

Mass Flux

Use the **Mass Flux** node to specify the mass flux into or out of the model domain through some of its boundaries. It is often possible to determine the mass flux from the pumping rate or from measurements. With this boundary condition, positive values correspond to flow into the model domain:

$$\mathbf{n} \cdot \rho \frac{\kappa}{\mu}(\nabla p + \rho g \nabla D) = N_0$$

where N_0 is a value or expression for the specified inward (or outward) Darcy flux. D is the elevation head which is set to zero for other than Subsurface Flow Module applications.

MASS FLUX

Enter a value or expression for the **Inward mass flux** N_0. A positive value of N_0 represents an inward mass flux whereas a negative value represents an outward mass flux. The units are based on the geometric entity: **Boundaries**: (SI unit: $\text{kg}/(\text{m}^2 \cdot \text{s})$).

Line Mass Source

The **Line Mass Source** node adds mass flow originating from a tube of infinitely small radius.

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
3D	Edges

LINE MASS SOURCE

Enter a value or expression for the source strength, N_0 (SI unit: $\text{kg}/(\text{m} \cdot \text{s})$). A positive value results in mass injection from the line into the computational domain, and a negative value means that the mass 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.

Fracture Flow

The equivalent feature available for fracture flow is the **Mass Source** attribute of the Fracture boundary condition and the **Mass Source** point feature of the Fracture Flow Interface, both available in 3D only.

Point Mass Source

The **Point Mass Source** node models mass flow originating from an infinitely small sphere centered around a point. It is available for points in 3D geometries.

POINT MASS SOURCE

Enter a value or expression for the source strength, N_0 (SI unit: kg/(s)). A positive value results in mass injection from the point into the computational domain, and a negative value means that the mass 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.

Inlet

The **Inlet** node adds a boundary condition for the inflow (or outflow) perpendicular (normal) to the boundary. It has three options that can be used to specify inlet condition on a boundary, as follows:

VELOCITY

Enter a value or expression for the **Normal inflow velocity** U_0 (SI unit: m/s). A positive value of U_0 represents an inflow velocity. A negative value represents an outflow velocity. The inlet velocity boundary condition is implemented as;

$$\mathbf{n} \cdot \rho \frac{\kappa}{\mu} (\nabla p + \rho g \nabla D) = \rho U_0$$

where U_0 is a value or expression for the specified inward (or outward) Darcy velocity. A positive value of the velocity U_0 corresponds to flow into the model domain whereas a negative value represents an outflow. D is the elevation head which is set to zero for other than Subsurface Flow Module applications.

PRESSURE

Use the **Pressure** option to specify the inlet pressure on a boundary. In many cases the distribution of pressure is known, giving a Dirichlet condition $p = p_0$ where p_0 is a known pressure given as a number, a distribution, or an expression involving time, t, for example. Enter a value or expression for the **Pressure** p_0 (SI unit: Pa).

MASS FLOW

If you select **Mass flow** as the inlet condition, specify the total **Mass flow rate** M_0 (SI unit: kg/s), or the **Pointwise mass flux** N_0 (SI unit: kg/(m^2·s)).

With **Mass flow rate** boundary condition, positive values correspond to flow into the model domain:

$$-\int_{\partial\Omega} \rho(\mathbf{u} \cdot \mathbf{n})\mathrm{d}S = M_0$$

where M_0 is a value or expression for the specified inward (or outward) Darcy flux.

Pointwise mass flux boundary condition, positive values correspond to flow into the model domain:

$$\mathbf{n} \cdot \rho\frac{\kappa}{\mu}(\nabla p + \rho g \nabla D) = N_0$$

where N_0 is a value or expression for the specified inward (or outward) Darcy flux.

CONSTRAINT SETTINGS

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

Symmetry

The **Symmetry** node describes a symmetry boundary. The following condition implements the symmetry condition on an axis or a flow divide:

$$\mathbf{n} \cdot \frac{\kappa}{\mu}\nabla p = 0$$

$$\mathbf{n} \cdot \frac{\kappa}{\mu}(\nabla p + \rho g \nabla D) = 0$$

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 the axial symmetry boundaries only.

No Flow

The **No Flow** node is the default boundary condition stating that there is no flow across impermeable boundaries. The mathematical formulation is:

$$\mathbf{n} \cdot \rho\frac{\kappa}{\mu}(\nabla p + \rho g \nabla D) = 0$$

where $\mathbf{n}$ is the vector normal to the boundary. D is the elevation head which is set to zero for any other than Subsurface Flow Module applications.

Flux Discontinuity

Use the **Flux Discontinuity** node to specify a mass flux discontinuity through an interior boundary. The condition is represented by the following equation:

$$-\mathbf{n} \cdot (\rho \mathbf{u}_1 - \rho \mathbf{u}_2) = N_0$$

In this equation, $\mathbf{n}$ is the vector normal (perpendicular) to the interior boundary, ρ is the fluid density, $\mathbf{u}_1$ and $\mathbf{u}_2$ are the Darcy velocities in the adjacent domains (as defined in Equation 6-13) and N_0 is a specified value or expression for the flux discontinuity.

$$\mathbf{u} = -\frac{\kappa}{\mu}\nabla p \qquad (6\text{-}13)$$

For this boundary condition, a positive value of N_0 corresponds to a flow discontinuity in the opposite direction to the normal vector of the interior boundary.

MASS FLUX

Enter a value or expression for the **Inward mass flux** N_0 (SI unit: $kg/(m^2{\cdot}s)$). A positive value of N_0 represents a mass flux discontinuity in the opposite direction to the normal vector of the interior boundary.

Outlet

The **Outlet** node adds a boundary condition for the outflow (or inflow) perpendicular (normal) to the boundary. It has different options that can be used to specify inlet condition on a boundary, as follows:

VELOCITY

Enter a value or expression for the **Normal outflow velocity** U_0 (SI unit: m/s). A positive value of U_0 represents an outflow velocity whereas a negative value represents an inflow velocity.

$$-\mathbf{n} \cdot \rho\frac{\kappa}{\mu}\nabla p = \rho U_0$$

where U_0 is a specified value or expression for the outward (or inward) Darcy velocity.

PRESSURE

Similar to the inlet **Pressure** option, the outlet pressure on a boundary can be specified. Enter a value or expression for the **Pressure** p_0 (SI unit: Pa).

Enter a value or expression for the discharge Q_D to specify the volumetric flow rate through the boundary. The mass flux $\rho\mathbf{u}$ is related to the discharge as follows:

$$\int_{\partial\Omega} \rho\mathbf{u} \cdot \mathbf{ds} = \rho Q_D. \tag{6-14}$$

The mean normal outflow velocity at the boundary can then be calculated as $U_{\text{out}} = Q_D/A$, where A is the cross sectional area of the boundary.

Precipitation

Enter a value or expression for the **Precipitation rate** which then contributes to the mass flux at the boundaries selected. If the boundary is inclined, a **Slope correction** can be applied.

Interior Wall

The **Interior Wall** boundary condition can only be applied on interior boundaries. It is similar to the **No Flux** boundary available on exterior boundaries except that it applies on both sides of an interior boundary. It allows discontinuities of velocity and pressure across the boundary. The **Interior Wall** boundary condition can be used to avoid meshing thin structures by applying no-flux condition on interior curves and surfaces instead.

Thin Barrier

The **Thin Barrier** boundary condition models interior permeable walls, membranes, geotextiles, or perforated plates as thin permeable barriers. The **Thin Barrier** boundary condition can only be applied on interior boundaries.

WALL

Enter a value or expression for the **Thickness** d_b (SI unit: m, the default is 0.1 m) and for the **Permeability** κ_b (SI unit: m^2). The default **Permeability** κ_b uses the value **From material**. For **User defined** select **Isotropic** to define a scalar value or **Diagonal**, **Symmetric**, or **Full** to define a tensor value and enter another value or expression in the field or matrix.

Pressure Head

Use the **Pressure Head** node to specify the pressure head (instead of the pressure) on a boundary. It adds this boundary condition for the pressure head $H_p = H_{p0}$, where H_{p0} is a known pressure head given as a number, a distribution, or an expression involving time, t, for example. The dimension of the pressure head is length (SI unit: m).

PRESSURE HEAD

Enter a value or expression for the **Pressure head** H_{p0} (SI unit: m). The default is 0 m.

CONSTRAINT SETTINGS

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

Hydraulic Head

Use the **Hydraulic Head** node to specify the hydraulic head (instead of the pressure) on a boundary. This adds the Dirichlet condition for the hydraulic head $H = H_0$ where H_0 is a known hydraulic head given as a number, a distribution, or an expression involving time, t, for example.

HYDRAULIC HEAD

Enter a value or expression for the **Hydraulic head** H_0 (SI unit: m). The default is 0 m.

CONSTRAINT SETTINGS

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

Atmosphere/Gauge

The **Atmosphere/Gauge** node specifies an atmospheric pressure or gauges the pressure to the atmospheric value. This means that the total hydraulic potential reduces to the gravitational pressure at the free surface. At a free surface, such as a spring or a seepage face, the pressure is atmospheric. If the pressures in the model is gauged to the atmospheric value ($p = 0$), the total hydraulic potential reduces to the gravitational potential at the free surface — for example, the height of the free surface multiplied by the fluid weight, or $\rho_f g D$. This boundary condition sets the pressure at the boundary to zero and $p = 0$.

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

Pervious Layer

The **Pervious Layer** node provides a boundary condition that describes a mass flux through a semi-pervious layer connected to an external fluid source at different pressure, pressure head, or hydraulic head. The model domain might connect to a larger body of water through the semi-pervious layer. This condition is represented with the following boundary condition:

$$\mathbf{n} \cdot \rho \frac{\kappa}{\mu}(\nabla p + \rho g \nabla D) = \rho R_b \left[\frac{(p_b - p)}{\rho g} + (D_b - D) \right] \qquad (6\text{-}15)$$

In this equation, p_b (SI unit: Pa) and D_b (SI unit: m) are the pressure and the elevation of the distant fluid source, respectively, and R_b (SI unit: 1/s) is the conductance of materials between the source and the model domain (conductance to flow in the semi-pervious layer adjacent to the boundary). Typically $R_b = K'/B'$, where K' is the hydraulic conductivity (SI unit: m/s) of the layer and B' (SI unit: m) is its thickness. Using logical relationships, it is possible to activate these expressions at different times or under various flow conditions.

When the pressure head H_p is specified instead of the pressure, the boundary condition is the following:

$$\mathbf{n} \cdot \rho K \nabla(H_p + D) = \rho R_b [(H_{pb} - H_p) + (D_b - D)] \qquad (6\text{-}16)$$

H_{pb} is the pressure head (SI unit: m) at the edge of the layer.

When the hydraulic head H is specified instead of the pressure head, the boundary condition becomes:

$$\mathbf{n} \cdot \rho K \nabla H = \rho R_b [H_b - H] \qquad (6\text{-}17)$$

H_b is the hydraulic head (SI unit: m) at the edge of the layer.

K in Equation 6-16 and Equation 6-17 is the hydraulic conductivity.

At a free surface, such as a water table or seepage face, the pressure is atmospheric (here taken to be zero), so the total hydraulic potential equals gravitational potential, which is defined on D.

> 💡 Gravity effects are not active by default. Select the check box **Include gravity** to activate the acceleration of gravity. Setting the elevation D to zero also turns off gravity effects.

PERVIOUS LAYER

Specify the material properties whether to specify an external pressure, pressure head, or hydraulic head.

Select an **External variable to specify** — **Pressure and elevation** to specify the external pressure, **Pressure head and elevation** to specify the external pressure head, or **Hydraulic head**. For all selections, enter a value for the **Conductance** R_b (SI unit: 1/s).

- For **Pressure and elevation** enter an **External pressure** p_b (SI unit: Pa) and **External elevation** D_b (SI unit: m).
- For **Pressure head and elevation** enter an **External pressure head** $H_{p\mathrm{b}}$ (SI unit: m), $H_{p\mathrm{b}}$ (SI unit: m) and **External elevation** D_b (SI unit: m).
- For **Hydraulic head** enter the **Hydraulic head** H_b (SI unit: m).

Well

The **Well** feature is intended to model injection or production wells and is available with the Subsurface Flow Module.

WELL

Enter a value or expression for the **Well diameter** d_w (SI unit: m, the default is 0.1 m). Select the **Well type** from the list: **Production** or **Injection**.

Specify either the **Pressure** (SI unit: Pa), **Pressure head** (SI unit: m), **Hydraulic head** (SI unit: m), or the **Mass flow**. If you select **Mass flow**, specify the total **Mass flow rate** (SI unit: kg/s), the **Mass flow rate per unit length** (SI unit: kg/(m·s)) or the **Mass flux** (SI unit: kg/(m^2·s)).

Fracture

Use the **Fracture** node to model flow along a boundaries representing fractures within a porous medium. By default, it adds the tangential form of the continuity equation and of Darcy's Law.

$$d_f \frac{\partial}{\partial t}(\varepsilon_p \rho) + \nabla_T \cdot (d_f \rho \mathbf{u}) = d_f Q_m \qquad (6\text{-}18)$$

$$\mathbf{u} = -\frac{\kappa}{\mu} \nabla_T p \qquad (6\text{-}19)$$

The **Fracture** feature has two default subfeatures — the Fluid (Fracture) subfeature where the fluid density ρ (SI unit: kg/m^3) and dynamic viscosity μ (SI unit: Pa·s) are defined and the Fracture Material subfeature where the permeability κ (SI unit: m^2) and porosity ε_p (dimensionless) are specified.

COORDINATE SYSTEM SELECTION

Select a coordinate system from the **Coordinate system** list for the interpretation of directions in anisotropic material properties. The default is the **Global coordinate system**, and the list contains any additional orthonormal coordinate system (except boundary coordinate systems) added under the **Definitions** node.

The subnodes inherit these coordinate system settings. In particular, the **Permeability** or **Hydraulic conductivity** (in the Fracture Material subnode) should be set according to the coordinate system selected in this section.

APERTURE

Enter a value for the **Fracture thickness** d_f.

FLOW MODEL

Define if the flow follows a linear or nonlinear pressure-velocity relationship.

- **Darcian flow** (default) defines a linear relationship using Equation 6-18 and Equation 6-19.

- **Non-Darcian flow** defines a nonlinear relationship using Equation 6-18 and the pressure-velocity relationship

$$\nabla_{\text{T}} p \ = \ -\frac{\mu}{\kappa}\mathbf{u} - \beta\rho|\mathbf{u}|\mathbf{u}$$

where the nonlinear parameter β (SI unit: $1/\text{m}$) is further specified in the Fracture Material subfeature.

STORAGE MODEL

Equation 6-18 can also be formulated with respect to a storage term.

$$\rho S\frac{\partial p}{\partial t} + \nabla \cdot \rho\left[-\frac{\kappa}{\mu}(\nabla p)\right] \ = \ Q_{\text{m}}$$

The storage coefficient S can be interpreted as the weighted compressibility of the porous material and the fluid. Define the time dependent storage term by selecting one of the following options from the drop-down menu:

- **From density and porosity** (default), uses the formulation of Equation 6-18
- **Linearized storage**, where the following linear equation is used to define the storage:

$$S \ = \ \varepsilon_{\text{p}}\chi_{\text{f}} + (1 - \varepsilon_{\text{p}})\chi_{\text{p}}$$

- **User defined** to directly specify the storage coefficient S

🔍
- About Darcian and Non-Darcian Flow in the *Porous Media Flow Module User's Guide*
- Storage Models in the *Subsurface Flow Module User's Guide*

FRACTURE MODEL

Choose between two options to model fractures that have different characteristics.

- **Highly conductive fracture** represents a fracture filled with a highly permeable material.
- **Thin conducting barrier** represents a fracture that is filled with a low permeable material and therefore acts as a barrier for the flow which adds a jump in the pressure across the boundary:

$$-\mathbf{n}_{u,d} \cdot (\rho \mathbf{u})_{u,d} = \rho \frac{(p_{d,u} - p_{u,d})}{d_b} \frac{\kappa_b}{\mu}$$

The barrier thickness d_b and permeability κ_b are defined in the Fracture Material subnode.

In addition, either on the upside, downside, or on both sides a highly conductive fracture material is present and Equation 6-18 and Equation 6-19 are solved for the highly conductive side. Further specifications are done in the Fracture Material subnode.

	Note that the option to specify the **Fracture Model** is only available for the Fracture feature within the Darcy's Law interface.

For the Fracture boundary node several subnodes are available from the context menu (right-click the parent node) or from the **Physics** toolbar, **Attributes** menu. As they are almost identical to the boundary conditions of the Fracture Flow interface, see Domain, Boundary, Edge, Point, and Pair Nodes for the Fracture Flow Interface in the *Subsurface Flow User's Guide* for further description. Note that **Precipitation** is only available for the Fracture Flow interface.

	This feature requires a specific license. For a detailed overview of the functionality available in each product, visit https://www.comsol.com/products/specifications/.

	Flow in a Fractured Reservoir: Application Library path **Subsurface_Flow_Module/Fluid_Flow/fractured_reservoir_flow**

Fluid (Fracture)

This node defines the material properties of the fluid of the Fracture parent node. The fluid can be specified as general gas or liquid or as an ideal gas.

MODEL INPUT

This section contains fields and values that are inputs for expressions defining material properties. If such user-defined property groups are added, the model inputs appear here.

FLUID PROPERTIES

The available options for the **Fluid type** are **Gas/Liquid** (default) or **Ideal gas**. The selection determines how the density and compressibility of the fluid are set. The latter is only required if a linearized storage model has been selected in the parent Fracture node. For all fluid types specify the dynamic viscosity μ (SI unit: Pa·s).

Gas/Liquid
This option specifies the **Density** and the **Compressibility** for a general gas or liquid.

Ideal Gas
For **Ideal gas** it uses the ideal gas law to describe the fluid. In this case, specify the thermodynamics properties. Select a **Gas constant type** — **Specific gas constant** R_s (the default) or **Mean molar mass** M_n (SI unit: J/(mol·K)). For **Mean molar mass** the universal gas constant $R = 8.314$ J/(mol·K) is used as the built-in physical constant. For both properties, the defaults use values **From material**. For **User defined** enter another value or expression.

If required by a **Storage Model**, the **Compressibility** of the ideal gas is calculated as $\chi_f = 1/p_A$ with the absolute pressure p_A (Pa).

	If **Hydraulic conductivity** is selected as the **Permeability model** (see the Fracture Material section), dynamic viscosity is not available. The hydraulic conductivity is defined using a combination of fluid and fracture material properties and replaces the need of defining the dynamic viscosity.

Fracture Material

This node defines the porosity and material properties of the solid matrix of the Fracture parent node.

MODEL INPUT
This section contains fields and values that are inputs for expressions defining material properties. If such user-defined property groups are added, the model inputs appear here.

BARRIER PROPERTIES
This section appears if the **Thin conducting barrier** option for the **Fracture model** is chosen in the parent Fracture feature.

Enter the values for the barrier thickness d_b and permeability κ_b.

Note that the **Thin Conductive barrier** option is only available for the Fracture feature within the Darcy's Law interface.

FRACTURE MATERIAL PROPERTIES

If the **Thin conducting barrier** option for the **Fracture model** is chosen in the parent Fracture feature you can specify the **Conductive layer position** here. Choose between **Both sides**, **Upside**, and **Downside**. A sketch above shows the position of conductive layers and barrier within the fracture.

The **Porosity** ε_p of the fracture material is taken **From material** by default. Select **User defined** to enter a value or expression for ε_p.

If required by a **Storage model** in the parent node, specify the **Effective compressibility** of the porous matrix. The default value is $\chi_p = 10^{-4}$ 1/Pa.

Select a **Permeability model** to specify the capacity of the fracture material to transmit flow. Which options are available depends on the **Flow model** setting in the parent node.

- Select **Permeability** (default) to define the permeability of the fracture material.

- Select **Hydraulic conductivity** or define a combination of fluid permeability and dynamic viscosity. For **Hydraulic conductivity** K (SI unit: m/s) select **Isotropic** to define a scalar value or **Diagonal** or **Symmetric** to define a tensor value. The default is $2.94 \cdot 10^{-4}$ m/s.

- Select **Cubic law** to define the permeability from the fracture thickness specified in the parent node and the roughness factor f_f.

If the Non-Darcian Flow Model is selected in the parent Fracture feature enter a value for the **Inertial resistance coefficient** β.

$\mathbb{Q}$	• About Darcian and Non-Darcian Flow in the *Porous Media Flow Module User's Guide* • Permeability Models in the *Porous Media Flow Module User's Guide*

The Free and Porous Media Flow, Brinkman Interface

The **Free and Porous Media Flow, Brinkman (fp)** interface (▦) is found under the **Porous Media and Subsurface Flow** branch (▦) when adding a physics interface. It is used to compute fluid velocity and pressure fields of single-phase flow where free flow is connected to porous media. The Free and Porous Media Flow, Brinkman interface is used over at least two different domains: a free channel and a porous medium. The physics interface is well suited for transitions between slow flow in porous media, governed by the Brinkman equations, and fast flow in channels described by the Navier–Stokes equations. Fluids with varying density can be included at Mach numbers below 0.3. Also the viscosity of a fluid can vary, for example, to describe non-Newtonian fluids. The physics interface can be used for stationary and time-dependent analyses.

When this physics interface is added, the following default nodes are also added in the **Model Builder** — **Fluid Properties**, **Wall**, and **Initial Values**. Then, from the **Physics** toolbar, add a **Porous Medium** node to be used on the domain selection corresponding to the porous media, or add other nodes that implement, for example, boundary conditions and volume forces. You can also right-click **Free and Porous Media Flow, Brinkman** 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 `fp`.

PHYSICAL MODEL

Compressibility
By default the physics interface uses the **Incompressible flow** formulation of the Navier–Stokes and Brinkman equations to model constant density flow. If required, select

Weakly compressible flow from the **Compressibility** list, to account for small variations in the density, which are only dependent on the temperature (nonisothermal flow) or **Compressible flow (Ma<0.3)** for fully compressible flow. However, for the flow modeled with this physics interface, the Mach number must be below 0.3.

Swirl Flow
For 2D axisymmetric components, select the **Swirl flow** check box to include the swirl velocity component, that is the velocity component u_φ in the azimuthal direction. While u_φ can be nonzero, there can be no gradients in the φ direction. Note that this feature is only available for specific modules. Visit https://www.comsol.com/products/specifications/ for a detailed overview.

Neglect Inertial Term
Select the **Neglect inertial term (Stokes flow)** check box if the inertial forces are small compared to the viscous forces.

Enable porous media domains
The **Enable porous media domains** check box is selected by default to solve the Brinkman equations in porous domains. If it is unchecked, the **Porous Medium** node is no longer available in this interface.

Include Gravity
Gravity is not included by default. Select the **Include gravity** check box to activate the acceleration of gravity. This automatically adds a global **Gravity** feature node to the interface model tree, and the buoyancy force is included in the Equations.

Also, when the **Include gravity** check box is selected, the **Use reduced pressure** option changes the pressure formulation from using the total pressure (default) to using the reduced pressure. This option is suitable for configurations where the density changes are very small; otherwise, the default formulation can be used. For more information, see Gravity.

Porous Treatment of No Slip Condition
Choose how the **No Slip** condition on internal boundaries should be treated. The options are **Standard no slip formulation** and **Porous slip** (default). The latter option provides a unified treatment when the porous matrix is fully resolved as well as when it is under resolved ensuring a smooth transition between regions with different resolutions; see No Slip under Wall in the The Laminar Flow and Creeping Flow Interfaces section.

Reference Pressure Level
Enter a **Reference pressure level** p_{ref} (SI unit: Pa). The default value is 1[atm].

Reference Temperature
Enter a **Reference temperature** T_{ref} (SI unit: K). The default value is 293.15[K].

Reference Position
If **Include gravity** is selected, a **Reference position** r_{ref} (SI unit: m) can be specified which is then used for the calculation of the hydrostatic pressure.

TURBULENCE
Turbulent flow can be simulated by changing the **Turbulence model type** to **RANS** (Reynolds-Averaged Navier–Stokes) or **Large Eddy Simulation** (which is only available in 3D). If turbulent flow is activated, you can choose from different **Turbulence model**s and options for **Wall treatment**. For a description of the different turbulence models, wall treatment options, and turbulence model parameters see Theory for the Turbulent Flow Interfaces in the *CFD Module User's Guide*.

DEPENDENT VARIABLES
The following dependent variables (fields) are defined for this physics interface — the **Velocity field u** (SI unit: m/s) and its components, and the **Pressure** p (SI unit: Pa).

🔍	• Domain, Boundary, Point, and Pair Nodes for the Free and Porous Media Flow, Brinkman Interface • Theory for the Free and Porous Media Flow, Brinkman Interface

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▦	*Current Density Distribution in a Solid Oxide Fuel Cell*: Application Library path **Fuel_Cell_and_Electrolyzer_Module/Fuel_Cells/sofc_unit_cell**

Domain, Boundary, Point, and Pair Nodes for the Free and Porous Media Flow, Brinkman Interface

The Free and Porous Media Flow, Brinkman Interface has the following domain, boundary, 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.

- Electrode Surface Coupling
- Fluid Properties
- Gravity
- Initial Values
- Porous Electrode Coupling

- Porous Medium
- Mass Source
- Volume Force
- Wall

Note that some features are only available with certain COMSOL products (see https://www.comsol.com/products/specifications/).

The following nodes (listed in alphabetical order) are described for the Laminar Flow interface in the *COMSOL Multiphysics Reference Manual*:

- No Viscous Stress
- Flow Continuity
- Inlet
- Line Mass Source
- Outlet

- Open Boundary
- Periodic Flow Condition
- Point Mass Source
- Pressure Point Constraint
- Symmetry

!	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.

Fluid Properties

Use the **Fluid Properties** node to define the fluid material, density, and dynamic viscosity.

The default **Fluid material** uses the **Domain material** (the material defined for the domain). Select another material as needed.

The default **Density** ρ (SI unit: kg/m^3) uses values **From material** based on the **Fluid material** selection. For **User defined** enter another value or expression. The default is 0 kg/m^3.

The **Dynamic viscosity** μ (SI unit: Pa·s) uses values **From material** based on the **Fluid material** selection. For **User defined** enter another value or expression. The default is 0 Pa·s.

Porous Medium

The **Porous Medium** node adds the Brinkman equations (excluding any mass sources) to the interface. It has two default subfeatures — the Fluid subfeature where the fluid density ρ(SI unit: kg/m^3) and dynamic viscosity μ (SI unit: Pa·s) are defined and the Porous Matrix subfeature where the permeability κ (SI unit: m^2) and porosity ε_p (dimensionless) are specified.

FLOW MODEL

Define if the flow follows a linear or nonlinear pressure-velocity relationship.

- **Darcian flow** (default) defines a linear relationship characteristic for low Reynolds number laminar flows.

- **Non-Darcian flow** defines a nonlinear relationship due to inertial or turbulence effects.

POROUS MEDIUM TURBULENCE MODEL

Defines a model which complements the basic turbulence model and accounts for the influence of the porous matrix on turbulent flow in Porous Media.

- **Default** and **Nakayama-Kuwahara** specify **Coefficient of subgrid turbulence generation by porous matrix** C_{stpm} which by default is set to 0.212.

- **Pedras-de Lemos** asks to specify **Choice of the Pedras-de Lemos model coefficient**. When **User defined** is chosen, specify **Coefficient of subgrid turbulence generation by porous matrix** C_{stpm} with default value 0.212. Choosing **Original** results in $C_{stpm} = 0.28 \cdot \sqrt{\varepsilon_p}$, while choosing **Recalibrated** results in $C_{stpm} = 0.18$.

Fluid

This node defines the material properties of the fluid of the Porous Medium parent node.

MODEL INPUT

This section contains fields and values that are inputs for expressions defining material properties. If such user-defined property groups are added, the model inputs appear here.

FLUID PROPERTIES

Specify the **Density** ρ and the **Dynamic viscosity** μ (SI unit: Pa·s) of the fluid. The defaults use values **From material**, for **User defined** enter a value or expression.

The dynamic viscosity describes the relationship between the shear stresses and the shear rate in a fluid. Intuitively, water and air have a low viscosity, and substances often described as thick, such as oil, have a higher viscosity.

Porous Matrix

This node defines the porosity and material properties of the solid matrix of the Porous Medium parent node.

MODEL INPUT

This section contains fields and values that are inputs for expressions defining material properties. If such user-defined property groups are added, the model inputs appear here.

MATRIX PROPERTIES

The **Porosity** ε_p (a dimensionless number between 0 and 1) uses by default the value **From material**. For **User defined** the default value is 1 which is equivalent to free flow.

Select a **Permeability model** to specify the capacity of the porous material to transmit flow. Depending on the **Flow model** selection in the parent **Porous Medium** feature node you can choose between the following options:

- **Permeability** (the default) to directly enter the permeability of the porous matrix or **Kozeny-Carman** to define the permeability from the porosity and mean **Particle diameter** for **Darcian** flow or

- **Forchheimer** or **Ergun** for **Non-Darcian** flow.

Note that some of these options are only available for certain modules. For a detailed overview of the functionality available in each product, visit https://www.comsol.com/products/specifications/.

The default **Permeability** κ (SI unit: m^2) uses the value **From material**, as defined by the **Porous material** list. For **User defined** select **Isotropic** to define a scalar value or **Diagonal** or **Symmetric** to define a tensor value.

For **Kozeny-Carman**, enter the mean **Particle diameter** d_p (SI unit: m), the default value is 0.5 mm.

In case a **Non-Darcian** flow model is chosen in the parent node, **Forchheimer** is the default selection for the **Permeability model**. For **Forchheimer**, the default **Permeability** κ (SI unit: m^2) uses the value **From material**. Furthermore, the dimensionless **Forchheimer parameter** c_F can be defined. The default value is 0.55.

If **Ergun** is selected, enter the mean **Particle diameter** d_p (default value: 0.5 mm). The permeability κ is then calculated using Equation 2-4 in the *Porous Media Flow Module User's Guide*.

$^{\text{Q}}$
- About Darcian and Non-Darcian Flow in the *Porous Media Flow Module User's Guide*
- Permeability Models in the *Porous Media Flow Module User's Guide*

Mass Source

Enter a value or expression for an optional mass source (or sink) **Source term** Q_m (SI unit: kg/(m^3·s)). This term accounts for mass deposit or mass creation within porous domains. The physics interface assumes that the mass exchange occurs at zero velocity.

Effective Mass Transport Parameters

A correction factor (**Bruggeman**, **No Correction**, or **User defined**) to the mass transport parameters (defined in the **Transport Properties** node) can be applied for the porous domain. Species diffusivities and mobilities are automatically adjusted by the porous media corrections. For **User defined** enter a value or expression for the **Conversion factor** f_{eff}. The default is 1. Species diffusivities and mobilities are automatically adjusted by the porous media corrections.

Volume Force

The **Volume Force** node specifies the force **F** on the right-hand side of the Navier–Stokes or Brinkman equations, depending on whether a Fluid Properties or Porous Medium node is active on the domain. It then acts on each fluid element in the specified domains.

VOLUME FORCE
Enter the components of the **Volume force F** (SI unit: N/m^3).

Porous Electrode Coupling

Use the **Porous Electrode Coupling** node to define a mass source based on the volumetric current densities of one or multiple Porous Electrode Reaction nodes in an Electrochemistry interface.

The source (or sink) is proportional to the **Molar mass (kg/mol)** of the reacting species, the current densities and the stoichiometric coefficients according to Faraday's law as defined by summation over the Reaction Coefficient subnodes.

SPECIES
Based on the number of species required for the model, use the **Add** ($+$) and **Delete** $\equiv$) buttons under the table to add or remove **Species**. Then enter a value for the **Molar mass (kg/mol)** in the applicable rows for each species.

The setting in the table will determine the number of available fields for entering the stoichiometric coefficients of the Reaction Coefficient subnodes.

Initial Values

The **Initial Values** node adds initial values for the velocity field and the pressure that can serve as an initial condition for a transient simulation or as an initial guess for a nonlinear solver.

INITIAL VALUES
Enter initial values or expressions for the **Velocity field u** (SI unit: m/s) and for the **Pressure** p (SI unit: Pa). The default values are 0 m/s and 0 Pa, respectively.

Gravity

The **Gravity** global feature is automatically added when **Include gravity** is selected at the interface level in the **Physical Model** settings. It defines the gravity forces from the **Acceleration of gravity** value. When a turbulence model that solves for the turbulent kinetic energy, k, is used, the option **Include buoyancy-induced turbulence** is available. When selected, the **Buoyancy contribution** is by default set to **Automatic from multiphysics**. Contributions are only obtained from multiphysics couplings that support buoyancy-induced turbulence, such as Nonisothermal Flow. If the **Buoyancy contribution** is switched to **User defined**, a text field for the **Turbulent Schmidt number** appears. See also Theory for Buoyancy-Induced Turbulence in the *CFD Module User's Guide*.

This feature requires a specific license. For a detailed overview of the functionality available in each product visit https://www.comsol.com/products/specifications/.

ACCELERATION OF GRAVITY

The **Acceleration of gravity** (SI unit m/s, default value $-g_{const}\mathbf{e_z}$ in 2D axial symmetry and 3D and $-g_{const}\mathbf{e_y}$ in 2D) is used to define the gravity forces. It should be a global quantity.

*Electrode-Electrolyte Interface Coupling*

Use the **Electrode-Electrolyte Interface Coupling** node to define a combined wall and inflow/outflow boundary condition based on current densities of one or multiple Electrode Reaction nodes in an Electrochemistry interface.

The flow is proportional to the **Molar mass (kg/mol)** of the reacting species, the current densities and the stoichiometric coefficients according to Faraday's law as defined by summation over the Reaction Coefficient subnodes.

TANGENTIAL VELOCITY CONDITION

For information about this section, see the Wall node. **No slip** is the default, but **Slip** may in some cases be a more applicable, for instance if a gas diffusion electrode is modeled as a boundary condition.

SPECIES

Based on the number of species required for the model, use the **Add** (+) and **Delete** ☰) buttons under the table to add or remove **Species**. Then enter a value for the **Molar mass (kg/mol)** in the applicable rows for each species.

The setting in the table will determine the number of available field for entering the stoichiometric coefficients of the Reaction Coefficient subnodes.

Wall

The **Wall** node includes a set of boundary conditions describing fluid-flow conditions at stationary, moving, and leaking walls.

BOUNDARY CONDITION

Select a **Boundary condition** for the wall.

- No Slip[1]
- Slip
- Leaking Wall

No Slip

No slip is the default boundary condition for a stationary solid wall for laminar flow (and SST, Low Re k-ε, Algebraic yPlus, L-VEL, and Spalart–Allmaras turbulence models). The condition prescribes $\mathbf{u} = 0$; that is, the fluid at the wall is not moving.

Slip

The **Slip** option prescribes a no-penetration condition, $\mathbf{u} \cdot \mathbf{n} = 0$. It is implicitly assumed that there are no viscous effects at the slip wall and hence, no boundary layer develops. From a modeling point of view, this can be a reasonable approximation if the main effect of the wall is to prevent fluid from leaving the domain.

Leaking Wall

This boundary condition may be used to simulate a wall where fluid is leaking into or leaving the domain with the velocity $\mathbf{u} = \mathbf{u}_l$ through a perforated wall. The components of the **Fluid velocity $\mathbf{u}_l$** on the leaking wall should be specified.

CONSTRAINT SETTINGS

This section is displayed by clicking the **Show** button (👁) and selecting **Advanced Physics Options**.

⚲	• The Moving Mesh Interface in the *COMSOL Multiphysics Reference Manual*

The Free and Porous Media Flow, Darcy Interface

The **Free and Porous Media Flow, Darcy** interface ( ) combines the **Darcy's Law** and **Laminar Flow** interfaces to compute fluid velocity and pressure fields where free flow is connected to porous media. The physics interface is suited for situations when both the free flow and the flow in the porous media are laminar.

When a predefined **Free and Porous Media Flow, Darcy** interface is added from the **Porous Media and Subsurface Flow** branch ( ) of the **Model Wizard** or **Add Physics** window, the **Darcy's Law** and **Laminar Flow** interfaces are added to the Model Builder. In addition, the **Multiphysics** node is added, which automatically includes the **Free and Porous Media Flow Coupling** multiphysics coupling.

On the Constituent Physics Interfaces

The **Darcy's Law** interface is used to simulate fluid flow through interstices in a porous medium. It can be used to model low-velocity flows in media where the permeability and porosity are very small, and for which the pressure gradient is the major driving force and the flow is mostly influenced by the frictional resistance within the pores.

The **Laminar Flow** interface is used to compute the velocity and pressure for a fluid flow in the laminar flow regime. A flow will remain laminar as long as the Reynolds number is below a certain critical value. At higher Reynolds numbers, disturbances have a tendency to grow and cause transition to turbulence.

SETTINGS FOR PHYSICS INTERFACES AND COUPLING FEATURES

When physics interfaces are added using the predefined couplings, for example **Free and Porous Media Flow, Darcy**, specific settings are included with the physics interfaces and the coupling features.

However, if physics interfaces are added one at a time, followed by the coupling features, these modified settings are not automatically included.

Free and Porous Media Flow Coupling (Multiphysics Coupling)

The **Free and Porous Media Flow Coupling** multiphysics coupling node ( ) bidirectionally links the **Laminar Flow** and **Darcy's Law** interfaces.

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 `nsd1`.

DOMAIN SELECTION

When nodes are added from the context menu, you can select **Manual** (the default) from the **Selection** list to choose specific domains to define the multiphase flow coupling, or select **All domains** as needed.

When the **Free and Porous Media Flow Coupling** is added as an effect of adding a Free and Porous Media Flow, Darcy multiphysics interface, the selection is the intersection of the boundaries of the participating physics interfaces.

Only boundaries that are active in the participating physics interfaces (which are chosen from the **Coupled Interfaces** selection list) can be selected.

COUPLED INTERFACES

This section defines the physics involved in the multiphysics coupling. The **Free flow** and **Porous media flow** lists include all applicable physics interfaces.

The default values depend on how the 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 selected 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 Free and Porous Media Flow Coupling node from a physics interface. If the physics interface is removed from the **Model Builder**, for example **Darcy's Law** is deleted, then the **Porous media flow** list defaults to **None** as there is nothing to couple to.

This section defines the settings for the **Free flow boundary condition**.

- When **No slip** is selected, the tangential component of the fluid velocity at the free-porous interface on the free-flow side (computed in the **Free flow** interface) is set to zero.

- When **Continuous tangential velocity** is selected, the tangential velocity component of the flow on both sides of the free-porous interface is continuous. In addition, continuity of normal stresses and conservation of mass across the interface are ensured.

- When **Beavers-Joseph** is selected, the difference of the tangential velocity components of the flow on both sides of the free-porous interface is proportional to the shear stress at the free-porous interface on the free-flow side. For this option, enter a value or expression for the **Beavers and Joseph parameter** a_{BJ} (dimensionless) that determines the proportionality. In addition, select the check box **Use projected permeability** to use only the component of the permeability tensor in the direction of the difference of the tangential velocities on both sides of the interface, instead of the trace of the permeability tensor, in determining the proportionality.

- When **Beavers-Joseph-Saffman** is selected, the tangential velocity component of the flow at the free-porous interface on the free-flow side is proportional to the shear stress at the interface on the free-flow side. For this option also, enter a value or expression for the **Beavers and Joseph parameter** a_{BJ} (dimensionless) that determines the proportionality. In addition, select the check box **Use projected permeability** to use only the component of the permeability tensor in the direction of the difference of the tangential velocities on both sides of the interface, instead of the trace of the permeability tensor, in determining the proportionality.

- When **Viscous slip** is selected, the difference of the tangential velocity components of the flow on the free-flow side and a user-supplied interfacial velocity is proportional to the shear stress at the free-porous interface on the free-flow side. Enter values for the **Slip length** L_s (SI unit: m, the default is 1e-7 m), and an **Interfacial velocity** $\mathbf{u}_b$ (SI unit: m/s, the default is 0 m/s).

In all the above cases, additionally continuity of normal stresses and conservation of mass across the interface are ensured.

Q | Please find related information in the *CFD Module User's Guide*:
  |
  | • The Darcy's Law Interface
  |
  | • Theory for the Darcy's Law Interface
  |
  | • The Laminar Flow Interface
  |
  | • Theory for the Single-Phase Flow Interfaces
  |
  | • Theory for the Free and Porous Media Flow, Darcy Interface

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The Brinkman Equations Interface

The **Brinkman Equations (br)** interface ( ), found under the **Porous Media and Subsurface Flow** branch ( ) when adding a physics interface, is used to compute fluid velocity and pressure fields of single-phase flow in porous media in the laminar flow regime. The physics interface extends Darcy's law to describe the dissipation of the kinetic energy by viscous shear, similar to the Navier–Stokes equations. Fluids with varying density can be included at Mach numbers below 0.3. Also the viscosity of a fluid can vary, for example, to describe non-Newtonian fluids. To simplify the equations, select the Stokes–Brinkman flow feature to reduce the dependence on inertial effects when the Reynolds number is significantly less than 1. The physics interface can be used for stationary and time-dependent analyses.

The main node is the Porous Medium feature, which adds the Brinkman equations and provides interfaces for defining the fluid material and the porous matrix.

When this physics interface is added, the following default nodes are also added in the **Model Builder** — **Porous Medium**, **Wall** (the default boundary type, using **No slip** as the default boundary condition), and **Initial Values**. Then, from the **Physics** toolbar, add other nodes that implement, for example, boundary conditions and volume forces. You can also right-click **Brinkman Equations** to select physics features from the context menu.

The boundary conditions are essentially the same as for the Laminar Flow interface. Differences exist for the following boundary types: Outlet, Symmetry, Open Boundary, and Boundary Stress where the viscous part of the stress is divided by the porosity to appear as

$$\frac{1}{\varepsilon_p}\left\{\mu(\nabla\mathbf{u}+(\nabla\mathbf{u})^T)-\frac{2}{3}\mu(\nabla\cdot\mathbf{u})\mathbf{I}\right\}$$

In the *COMSOL Multiphysics Reference Manual* see Table 2-4 for links to common sections such as **Discretization**, **Consistent Stabilization**, **Inconsistent Stabilization**, and **Advanced Settings**, all accessed by clicking the **Show** button ( ) and choosing the applicable option. You can also search for information: press F1 to open the **Help** window or Ctrl+F1 to open the **Documentation** window.

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 `br`.

PHYSICAL MODEL

This node specifies the properties of the Brinkman Equations interface, which describe the overall type of fluid flow model.

Compressibility

By default the physics interface uses the **Incompressible flow** formulation of the Brinkman equations to model constant density flow. Alternatively, from the **Compressibility** list select **Weakly compressible flow**, which should be used when the pressure dependency of the density can be neglected, or **Compressible flow (Ma<0.3)** to solve for the full compressible flow of which, however, the Mach number must be below 0.3.

Swirl Flow

For 2D axisymmetric models, select the **Swirl flow** check box to include the swirl velocity component, that is the velocity component u_φ in the azimuthal direction. While u_φ can be nonzero, there can be no gradients in the φ direction.

Note that this feature is only available for specific modules. See https://www.comsol.com/products/specifications/ for a detailed overview.

Neglect Inertial Term (Stokes–Brinkman Flow)

The **Neglect inertial term (Stokes–Brinkman)** check box is selected by default to model flow at low Reynolds numbers for which the inertial term can be neglected. This results in the linear Stokes–Brinkman equations.

Include Gravity

Gravity is not included by default. Select the **Include gravity** check box to activate the acceleration of gravity. This automatically adds a global **Gravity** feature node to the interface model tree, and the buoyancy force is included in the Equations.

Also, when the **Include gravity** check box is selected, the **Use reduced pressure** option changes the pressure formulation from using the total pressure (default) to using the reduced pressure. This option is suitable for configurations where the density changes

are very small; otherwise, the default formulation can be used. For more information, see Gravity.

Porous Treatment of No Slip Condition
Choose how the **No Slip** condition on **Wall** boundaries and **Interior Wall** boundaries adjacent to **Porous Medium** should be treated. The options are **Standard no slip formulation** and **Porous slip** (default) . The latter option provides a unified treatment when the porous matrix is fully resolved as well as when it is under resolved ensuring a smooth transition between regions with different resolutions; see No Slip under Wall in the The Laminar Flow and Creeping Flow Interfaces section.

Reference Pressure Level
Enter a **Reference pressure level** p_{ref} (SI unit: Pa). The default value is 1[atm].

Reference Temperature Level
Enter a **Reference temperature level** T_{ref} (SI unit: K). The default value is 293.15[K].

Reference Position
If **Include gravity** is selected, a **Reference position** r_{ref} (SI unit: m) can be specified which is then used for the calculation of the hydrostatic pressure.

TURBULENCE

Turbulent flow can be simulated by changing the **Turbulence model type** to **RANS** (Reynolds-Averaged Navier–Stokes). If turbulent flow is activated, you can set the **Turbulence model** either to one of the algebraic turbulence models, **Algebraic yPlus** (the default) or **L-VEL**, or to one of the following two-equation turbulence models: k-ε, Low Reynolds Number k-ε. The **Wall treatment** is set to **Automatic** (default) or **Low Re** while **Wall functions** is the only option for k-ε. For more information about turbulence modeling, see Theory for the Turbulent Flow Interfaces in the *CFD Module User's Guide*.

DEPENDENT VARIABLES

The following dependent variables (fields) are defined for this physics interface — the **Velocity field u** (SI unit: m/s) and its components, and the **Pressure** p (SI unit: Pa).

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.

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.

Q

- Domain, Boundary, Point, and Pair Nodes for the Brinkman Equations Interface
- Theory for the Brinkman Equations Interface

In the *COMSOL Multiphysics Reference Manual*:

- Pseudo Time Stepping for Laminar Flow Models and Pseudo Time Stepping
- Numerical Stability — Stabilization Techniques for Fluid Flow
- Nitsche Constraints

Domain, Boundary, Point, and Pair Nodes for the Brinkman Equations Interface

The Brinkman Equations Interface has the following domain, boundary, 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:

- Porous Medium
- Initial Values
- Mass Source
- Volume Force
- Fluid Properties

The following nodes (listed in alphabetical order) are described for the Laminar Flow interface in the *COMSOL Multiphysics Reference Manual*:

- Flow Continuity
- Inlet
- Line Mass Source
- Boundary Stress
- Outlet
- Open Boundary

- Periodic Flow Condition
- Point Mass Source
- Pressure Point Constraint
- Symmetry
- Wall

> [!]
> 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.

Porous Medium

The **Porous Medium** node adds the Brinkman equations: Equation 4-34 and Equation 4-35 (excluding any mass sources). It has two default subfeatures — the Fluid subfeature where the fluid density ρ(SI unit: kg/m^3) and dynamic viscosity μ (SI unit: Pa·s) are defined and the Porous Matrix subfeature where the permeability κ (SI unit: m^2) and porosity ε_p (dimensionless) are specified.

COORDINATE SYSTEM SELECTION

Select a coordinate system from the **Coordinate system** list for the interpretation of directions in anisotropic material properties. The default is the **Global coordinate system**, and the list contains any additional orthonormal coordinate system (except boundary coordinate systems) added under the Definitions node.

The subnodes inherit these coordinate system settings. In particular, the **Permeability** (in the **Porous Matrix** subnode) should be set according to the coordinate system selected in this section.

FLOW MODEL

Define if the flow follows a linear or nonlinear pressure-velocity relationship.

- **Darcian flow** (default) defines a linear relationship characteristic for low Reynolds number laminar flows.

- **Non-Darcian flow** defines a nonlinear relationship due to inertial or turbulence effects.

POROUS MEDIUM TURBULENCE MODEL

If in the parent feature node a turbulence model other than **Algebraic yPlus** or **L-VEL** is selected, define a model which complements the basic turbulence model and accounts for the influence of the porous matrix on turbulent flow in porous media.

- For **Default** and **Nakayama-Kuwahara** specify the **Coefficient of subgrid turbulence generation by porous matrix** C_{stpm} which by default is set to 0.212.

- For **Pedras-de Lemos**, specify the **Choice of the Pedras-de Lemos model coefficient**. When **User defined** is chosen, specify the **Coefficient of subgrid turbulence generation by porous matrix** C_{stpm} with default value 0.212. Choosing **Original** results in $C_{stpm} = 0.28 \cdot \sqrt{\varepsilon_p}$, while choosing **Recalibrated** results in $C_{stpm} = 0.18$.

DISTANCE EQUATION

This section is available for the turbulence models **Algebraic yPlus** or **L-VEL**. Select how the **Reference length scale** l_{ref} (SI unit: m) is defined — **Automatic** (default) or **Manual**:

- For Automatic the wall distance is automatically evaluated to one tenth of the shortest side of the geometry bounding box. This is usually quite accurate but it can sometimes give a too high value if the geometry consists of several slim entities. In such cases, define the reference length scale manually.

- For Manual it defines a different value or expression for the length scale. The default is 1 m.

l_{ref} controls the result of the distance equation. Objects that are much smaller than l_{ref} are effectively be diminished while the distance to objects much larger than l_{ref} are accurately represented.

Fluid

This node defines the material properties of the fluid of the Porous Medium parent node.

MODEL INPUT

This section contains fields and values that are inputs for expressions defining material properties. If such user-defined property groups are added, the model inputs appear here.

FLUID PROPERTIES

Specify the **Density** ρ and the **Dynamic viscosity** μ (SI unit: Pa·s) of the fluid. The defaults use values **From material**, for **User defined** enter a value or expression.

The dynamic viscosity describes the relationship between the shear stresses and the shear rate in a fluid. Intuitively, water and air have a low viscosity, and substances often described as thick, such as oil, have a higher viscosity.

Porous Matrix

This node defines the porosity and material properties of the solid matrix of the Porous Medium parent node.

MODEL INPUT

This section contains fields and values that are inputs for expressions defining material properties. If such user-defined property groups are added, the model inputs appear here.

MATRIX PROPERTIES

The **Porosity** ε_p (a dimensionless number between 0 and 1) uses by default the value **From material**. For **User defined** the default value is 1.

Select a **Permeability model** to specify the capacity of the porous material to transmit flow. Depending on the **Flow model** selection in the parent **Porous Medium** feature node you can choose between the following options:

- **Permeability** (the default) to directly enter the permeability of the porous matrix or **Kozeny-Carman** to define the permeability from the porosity and mean **Particle diameter** for **Darcian** flow or

- **Forchheimer** or **Ergun** for **Non-Darcian** flow.

Note that some of these options are only available for certain modules. For a detailed overview of the functionality available in each product, visit https://www.comsol.com/products/specifications/.

The default **Permeability** κ (SI unit: m^2) uses the value **From material**, as defined by the **Porous material** list. For **User defined** select **Isotropic** to define a scalar value or **Diagonal** or **Symmetric** to define a tensor value.

For **Kozeny-Carman**, enter the mean **Particle diameter** d_p (SI unit: m), the default value is 0.5 mm.

In case a **Non-Darcian** flow model is chosen in the parent node, **Forchheimer** is the default selection for the **Permeability model**. For **Forchheimer**, the default **Permeability** κ (SI unit: m^2) uses the value **From material**. Furthermore, the dimensionless **Forchheimer parameter** c_F can be defined. The default value is 0.55.

If **Ergun** is selected, enter the mean **Particle diameter** d_p (default value: 0.5 mm). The permeability κ is then calculated using Equation 2-4 in the *Porous Media Flow Module User's Guide*.

🔍	• About Darcian and Non-Darcian Flow in the *Porous Media Flow Module User's Guide*
	• Permeability Models in the *Porous Media Flow Module User's Guide*

Mass Source

The **Mass Source** node adds a mass source (or mass sink) Q_m to the right-hand side of the continuity equation: Equation 6-72. This term accounts for mass deposit and/or mass creation in porous domains. The physics interface assumes that the mass exchange occurs at zero velocity.

$$\frac{\partial}{\partial t}(\varepsilon_p \rho) + \nabla \cdot (\rho \mathbf{u}) = Q_m \tag{6-20}$$

DOMAIN SELECTION
Only Porous Matrix domains are available.

MASS SOURCE
Enter a value or expression for the **Source term** Q_{br} (SI unit: kg/(m^3·s)). The default is 0 kg/(m^3·s).

Volume Force

Use the **Volume Force** node to specify the force **F** on the right-hand side of Equation 6-73. It then acts on each fluid element in the specified domains.

$$\frac{\rho}{\varepsilon_p}\left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\frac{\mathbf{u}}{\varepsilon_p}\right) =$$

$$-\nabla p + \nabla \cdot \left[\frac{1}{\varepsilon_p}\left\{\mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right\}\right] - \left(\kappa^{-1}\mu + \frac{Q_m}{\varepsilon_p^2}\right)\mathbf{u} + \mathbf{F} \tag{6-21}$$

VOLUME FORCE

Enter the components of **Volume force F** (SI unit: N/m^3).

Initial Values

The **Initial Values** node adds initial values for the velocity field and the pressure that can serve as an initial condition for a transient simulation or as an initial guess for a nonlinear solver.

INITIAL VALUES

Enter initial values or expressions for the **Velocity field u** (SI unit: m/s) and the **Pressure** p (SI unit: Pa). The default values are 0 m/s and 0 Pa, respectively.

Fluid Properties

The **Fluid Properties** node adds the momentum and continuity equations to solve for free flow in nonporous domains. The node also provides an interface for defining the material properties of the fluid.

MODEL INPUTS

Fluid properties, such as density and viscosity, can be defined through user inputs, variables, or by selecting a material. For the latter option, additional inputs — for example, temperature or pressure — may be required to define these properties.

Temperature

By default, the single-phase flow interfaces are set to model isothermal flow. Hence, the **Temperature** is **User defined** and defaults to 293.15 K. If a Heat Transfer interface is included in the component, the temperature may alternatively be selected from this 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.

Absolute Pressure

This input appears when a material requires the absolute pressure as a model input. The absolute pressure is used to evaluate material properties, but it also relates to the value of the calculated pressure field. There are generally two ways to calculate the pressure when describing fluid flow: either to solve for the absolute pressure or for a pressure (often denoted gauge pressure) that relates to the absolute pressure through a reference pressure.

The choice of pressure variable depends on the system of equations being solved. For example, in a unidirectional incompressible flow problem, the pressure drop over the modeled domain is probably many orders of magnitude smaller than the atmospheric pressure, which, when included, may reduce the stability and convergence properties of the solver. In other cases, such as when the pressure is part of an expression for the gas volume or the diffusion coefficients, it may be more convenient to solve for the absolute pressure.

The default **Absolute pressure** p_A is $p+p_{ref}$ where p is the dependent pressure variable from the Navier–Stokes equations, and p_{ref} is from the user input defined at the physics interface level. When p_{ref} is nonzero, the physics interface solves for a gauge pressure. If the pressure field instead is an absolute pressure field, p_{ref} should be set to 0.

The **Absolute pressure** field can be edited by clicking **Make All Model Inputs Editable** (🖾) and entering the desired value in the input field.

FLUID PROPERTIES

If density variations with respect to pressure are to be included in the computations, the flow must be set to compressible.

The **Dynamic viscosity** μ describes the relationship between the shear rate and the shear stresses in a fluid. Intuitively, water and air have low viscosities, and substances often described as thick (such as oil) have higher viscosities.

Gravity

The **Gravity** global feature is automatically added when **Include gravity** is selected at the interface level in the **Physical Model** settings. It defines the gravity forces from the **Acceleration of gravity** value. When a turbulence model that solves for the turbulent

kinetic energy, k, is used, the option **Include buoyancy-induced turbulence** is available. When selected, the **Buoyancy contribution** is by default set to **Automatic from multiphysics**. Contributions are only obtained from multiphysics couplings that support buoyancy-induced turbulence, such as Nonisothermal Flow. If the **Buoyancy contribution** is switched to **User defined**, a text field for the **Turbulent Schmidt number** appears. See also Theory for Buoyancy-Induced Turbulence in the *CFD Module User's Guide*.

This feature requires a specific license. For a detailed overview of the functionality available in each product visit https://www.comsol.com/products/specifications/.

ACCELERATION OF GRAVITY

The **Acceleration of gravity** (SI unit m/s, default value $-g_{const}\mathbf{e_z}$ in 2D axial symmetry and 3D and $-g_{const}\mathbf{e_y}$ in 2D) is used to define the gravity forces. It should be a global quantity.

The Multiphase Flow in Porous Media Interface

The **Multiphase Flow in Porous Media** interface ( ) combines the **Darcy's Law** interface with the **Phase Transport in Porous Media** interface to model the flow and transport of multiple immiscible phases in a porous medium.

When a predefined **Multiphase Flow in Porous Media** interface is added from the **Porous Media and Subsurface Flow** branch ( ) of the **Model Wizard** or **Add Physics** window, **Phase Transport** and **Darcy's Law** interfaces are added to the Model Builder. In addition, the **Multiphysics** node is added, which automatically includes the **Multiphase Flow in Porous Media** multiphysics coupling.

On the Constituent Physics Interfaces

The **Phase Transport in Porous Media** interface is used to simulate the transport of immiscible multiple species in a porous medium and solves for their averaged volume fractions (also called saturations). The interfaces between the different phases are not tracked explicitly, although microscopic interfacial effects are taken into account in the macroscopic equations through the capillary pressure functions.

The **Darcy's Law** interface is used to simulate fluid flow through interstices in a porous medium. It can be used to model low-velocity flows in media where the permeability and porosity are very small, and for which the pressure gradient is the major driving force and the flow is mostly influenced by the frictional resistance within the pores.

SETTINGS FOR PHYSICS INTERFACES AND COUPLING FEATURES

When physics interfaces are added using the predefined couplings, for example **Multiphase Flow in Porous Media**, specific settings are included with the physics interfaces and the coupling features.

However, if physics interfaces are added one at a time, followed by the coupling features, these modified settings are not automatically included.

For example, if single **Phase Transport in Porous Media** and **Darcy's Law** interfaces are added, an empty **Multiphysics** node appears in the model tree. You can choose from the available coupling features but the settings in the constituent interfaces are not modified.

Multiphase Flow in Porous Media (Multiphysics Coupling)

The **Multiphase Flow in Porous Media** multiphysics coupling node (🌐) links bidirectionally the **Phase Transport in Porous Media** and **Darcy's Law** interfaces.

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 mfpm1.

DOMAIN SELECTION

When nodes are added from the context menu, you can select **Manual** (the default) from the **Selection** list to choose specific domains to define the multiphase flow coupling, or select **All domains** as needed.

When **Multiphase Flow in Porous Media** is added as an effect of adding a Multiphase Flow in Porous Media interface, the selection is the same as for the participating physics interfaces.

Only domains that are active in the participating physics interfaces (which are chosen from the **Coupled Interfaces** selection list) can be selected.

COUPLED INTERFACES

This section defines the physics involved in the multiphysics coupling. The **Phase transport** and **Flow in porous media** lists include all applicable physics interfaces.

The default values depend on how the 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 selected 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 Multiphase Flow in Porous Media node from a physics interface. If the physics interface is removed from the **Model Builder**, for example **Darcy's Law** is deleted, then the **Flow in porous media** list defaults to **None** as there is nothing to couple to.

Please find related information under

- The Phase Transport Interfaces and
- Theory for the Phase Transport Interfaces

in the *CFD Module User's Guide*.

Well (Multiphysics Coupling)

The **Multiphase Flow in Porous Media** ( ) interface contains an optional **Well** multiphysics coupling feature on points (in 2D) or edges (in 3D). The **Well** coupling node is intended to model injection or production wells and links bidirectionally the **Phase Transport in Porous Media** and **Darcy's Law** interfaces.

The Subsurface Flow Module license is required to use this coupling feature (see https://www.comsol.com/products/specifications/).

SETTINGS
The **Label** is the default multiphysics coupling feature name.

The default **Name** (for the first **Well** multiphysics coupling feature in the model) is wellmpp1.

POINT OR EDGE SELECTION
When nodes are added from the context menu, you can select **Manual** (the default) from the **Selection** list to choose specific points or edges, or select **All points** or **All edges** as needed.

COUPLED INTERFACES
This section controls which individual interfaces are coupled by the current coupling feature. 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 correct physics interface again from the **Phase transport** or **Flow in porous media** lists

WELL

Select whether the well is a production or injection well: for an injection well positive mass fluxes signify inflowing fluxes and for a production well positive mass fluxes are outflowing fluxes.

Either specify the total **Total mass flow rate** M_0 (SI unit: kg/s), the **Total mass flow rate per unit length** M_1 (SI unit: kg/(m·s)), the **Pressure** p_0 (SI unit: Pa), the **Pressure head** H_{p0} (SI unit: m), or the **Hydraulic head** H_0 (SI unit: m). The elevation D used to convert the hydraulic head to a pressure, is defined by the gravity effects in the coupled Darcy's Law interface.

Select the **Specify well diameter** check box to define the **Well diameter** d_w (SI unit: m). This averages the mass source on the boundary of a cylinder around the line. This option avoids obtaining an increasing pressure value at the line when meshing finer than this diameter. It makes use of the `circavg` operator.

If the well diameter is defined, the option to specify the **Total mass flux** N_0 (SI unit: kg/(m^2·s)) is also available.

PHASES

The number of **Phase** sections depends on the number of phases defined in the coupled Phase Transport in Porous Media interface: the number of sections is equal to the number of phases not computed from the volume constraint, which is in turn equal to the number of phases defined in the coupled Phase Transport in Porous Media interface minus one.

Specify the boundary condition for each phase not computed from the volume constraint. You can choose to enter a value for the **Mass flow rate** $M_{0,i}$ (SI unit: kg/s), the **Mass flow rate per unit length** $M_{1,i}$ (SI unit: kg/(m·s)), or the **Volume fraction** $s_{0,i}$ (dimensionless). If the well diameter is specified, the option to specify the **Mass flux** $N_{0,i}$ (SI unit: kg/(m^2·s)) is also available. For a production well, you can additionally choose the **Outflow** option. For an injection well you can additionally choose to specify the **Fraction of total volumetric flow rate** $s_{0,i}$ (dimensionless).

Fraction of total volumetric flow rate
When the **Fraction of total volumetric flow rate** $s_{0,i}$ is specified for a phase, a mass flow rate per unit length $M_{1,i}$ is supplied for that phase, which is given by

$$M_{1,i} = \rho_i s_{0,i} V_1 \tag{6-22}$$

where V_1 is the total volumetric flow rate per unit length, which is computed as follows: assume that there are N phases, and that phase 1 is the phase computed from the

volume constraint, that for phases i, for $i = 2, ..., p$, the fraction of total volumetric flow rate $s_{0,i}$ is supplied, and that for the phases i, for $i = p+1, ..., N$, the mass flow rate per unit length $M_{1,i}$ is given. Then V_1 can be computed from the relation

$$V_1 = \frac{M_{1,1}}{\rho_1} + \sum_{i=2}^{p} V_1 s_{i,0} + \sum_{i=p+1}^{N} \frac{M_{1,i}}{\rho_i} \tag{6-23}$$

where the mass flow rate $M_{1,1}$ for the phase computed from the volume constraint is given by

$$M_{1,1} = M_1 - \sum_{i=2}^{p} V_1 \rho_i s_{i,0} - \sum_{i=p+1}^{N} M_{1,i} \tag{6-24}$$

Note that the total mass flow rate per unit length M_1 is readily available when any of the **Total mass flow rate**, **Total mass flow rate per unit length**, or the **Total mass flux** options is chosen. Furthermore, the total mass flow rate per unit length M_1 is also available as a Lagrange multiplier in case any of the **Pressure**, the **Pressure head**, or the **Hydraulic head** is given, as these conditions are implemented as weak constraints. For the mass flow rates per unit length $M_{1,i}$ of the individual phases, it holds similarly that they are readily available when any of the **Mass flow rate**, **Mass flow rate per unit length**, or the **Mass flux** options are chosen, and that for the **Volume fraction** option, implemented as a weak constraint, the mass flow rate per unit length $M_{1,i}$ is computed as a Lagrange multiplier.

Outflow

When the **Outflow** option is specified for a phase s_i, an outflowing mass flow rate per unit length $M_{1,i}$ is supplied for that phase, which is given by

$$M_{1,i} = \frac{\rho_i \kappa_{ri}}{\lambda_r \mu_i} M_1 \qquad \text{with} \quad \lambda_r = \sum_{i=1}^{N} \frac{\rho_i \kappa_{ri}}{\mu_i} \tag{6-25}$$

where κ_{ri} denotes the relative permeability of phase i.

Thin Barrier (Multiphysics Coupling)

The **Multiphase Flow in Porous Media** ( ) interface contains an optional **Thin Barrier** multiphysics coupling feature on edges (in 2D) or surfaces (in 3D). The **Thin Barrier** coupling node can be used to avoid meshing interior permeable structures that are less

permeable than the adjacent porous domains. It links bidirectionally the **Phase Transport in Porous Media** and **Darcy's Law** interfaces.

SETTINGS

The **Label** is the default multiphysics coupling feature name.

The default **Name** (for the first **Thin Barrier** multiphysics coupling feature in the model) is `tbls1`.

BOUNDARY SELECTION

When nodes are added from the context menu, you can select **Manual** (the default) from the **Selection** list to choose specific boundaries, or select **All boundaries** as needed.

COUPLED INTERFACES

This section controls which individual interfaces are coupled by the current coupling feature. 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 correct physics interface again from the **Phase transport** or **Flow in porous media** lists

SHELL PROPERTIES

The **Thin Barrier** multiphysics coupling feature is designed to be only applicable for a **Single Layer Material.** Select the **Single Layer Material** to be used for the thin barrier from the **Layer** list. The **Thickness** of the thin barrier is set in the **Layer Definition** section of the **Shell Property Group** window of the **Single Layer Material**. Also use this section to set the number of **Mesh elements** that are used in the Extra Dimension to solve the equations through the thickness of the thin barrier layer.

MODEL INPUT

The material properties of the different phases, such as density and viscosity, can be defined through user inputs, variables, or by selecting a boundary material. For the latter option, additional inputs, for example temperature or pressure, may be required to define these properties. These model inputs appear in this section.

MATRIX PROPERTIES

Select the material to use as porous matrix inside the thin barrier. Select **Boundary material** (the default) from the **Porous material** list to use the material defined for the thin barrier boundary. Select another material to use that material's properties.

The default **Porosity** ε_p (a dimensionless number between 0 and 1) uses the value **From material**, defined by the **Porous material** selected. For **User defined** the default is 0.5.

The default **Permeability** κ (SI unit: m^2) uses the value **From material**, as defined by the **Porous material** selected. For **User defined** the default is 1e-9 m^2.

CAPILLARY PRESSURE

Select a **Capillary pressure model** — **User defined** (the default), **van Genuchten**, **Brooks and Corey**, or **Capillary diffusion**. The **van Genuchten** and **Brooks and Corey** options are only available when there are not more than two phases present in the model.

- For **User defined**, enter an expression for the **Capillary pressure** p_c (SI unit: Pa) for the phases that are not computed from the volume constraint. The pressure of the corresponding phase is equal to the pressure of the phase computed from the volume constraint plus the capillary pressure supplied for this phase.

- For **van Genuchten**, enter an **Entry capillary pressure** p_{ec} (SI unit: Pa), the **Constitutive relations constant** m_{vG} (dimensionless), and **Constitutive relations constant** l_{vG} (dimensionless).

- For **Brooks and Corey**, enter an **Entry capillary pressure** p_{ec} (SI unit: Pa) and the **Pore size distribution index** λ_p (dimensionless).

- For **Capillary diffusion**, enter a capillary diffusion coefficient D_c (SI unit: m^2/s) for the phases that are not computed from the volume constraint.

PHASE PROPERTIES

Select the material to use for each phase. Select **Boundary material** (the default) from the **Fluid** list to use the material defined for the domain. Select another material to use that material's properties.

Enter the **Density** ρ (SI unit: kg/m^3), **Dynamic viscosity** μ (SI unit: Pa·s) and **Relative permeability** κ_r (a dimensionless number between 0 and 1) for each phase. The defaults for the **Density** and **Dynamic viscosity** are **From material**, and **User defined** for the **Relative permeability**. For **User defined**, the default values are 1000 kg/m^3, 0.001 Pa·s. and s_i^2, respectively.

The **Relative permeability** input fields are only available when the **Capillary pressure model** is set to **User defined** or **Capillary diffusion**. In the other cases (**van Genuchten** or **Brooks and Corey**) the relative permeabilities are defined by the **van Genuchten** or **Brooks and Corey** model. For the **van Genuchten** and **Brooks and Corey** model, specify the **Residual saturation** s_{ri} (dimensionless, default value 0) for each phase.

INITIAL VALUES

Enter a value or expression in the field for the volume fraction inside the thin barrier of each phase, except for the one computed from the volume constraint, and in the field for the pressure of the phase computed from the volume constraint.

Please find related information under

- Single Layer Materials in the *COMSOL Multiphysics Reference Manual* and
- Theory for the Multiphase Flow in Porous Media Interface in the *Subsurface Flow Module User's Guide*.

The Multiphase Free and Porous Media Flow Interface

The **Multiphase Free and Porous Media Flow** interface ( ) combines the **Phase Transport in Free and Porous Media** interface with the **Darcy's Law** and **Laminar Flow** interfaces to model the transport of multiple immiscible phases in coupled free and porous media flow.

When a predefined **Multiphase Free and Porous Media Flow** interface is added from the **Porous Media and Subsurface Flow** branch ( ) of the **Model Wizard** or **Add Physics** window, the **Phase Transport in Free and Porous Media, Darcy's Law** and **Laminar Flow** interfaces are added to the Model Builder. In addition, the **Multiphysics** node is added, which automatically includes the **Multiphase Flow in Porous Media**, the **Mixture Model**, and the **Free and Porous Media Flow Coupling** multiphysics couplings.

On the Constituent Physics Interfaces
The **Phase Transport in Free and Porous Media Flow** interface is used to simulate the transport of multiple immiscible species in free and porous media flow and solves for their averaged volume fractions (also called saturations). The interfaces between the different phases are not tracked explicitly, although microscopic interfacial effects are taken into account in the macroscopic equations through the capillary pressure functions in porous domains.

The **Darcy's Law** interface is used to simulate fluid flow through interstices in a porous medium. It can be used to model low-velocity flows in media where the permeability and porosity are very small, and for which the pressure gradient is the major driving force and the flow is mostly influenced by the frictional resistance within the pores.

The **Laminar Flow** interface is used to compute the velocity and pressure for a fluid flow in the laminar flow regime. A flow will remain laminar as long as the Reynolds number is below a certain critical value. At higher Reynolds numbers, disturbances have a tendency to grow and cause transition to turbulence.

SETTINGS FOR PHYSICS INTERFACES AND COUPLING FEATURES

When physics interfaces are added using the predefined couplings, for example **Multiphase Free and Porous Media Flow**, specific settings are included with the physics interfaces and the coupling features.

However, if physics interfaces are added one at a time, followed by the coupling features, these modified settings are not automatically included.

Coupling Features

Three coupling features are added: The Multiphase Flow in Porous Media (Multiphysics Coupling), the Free and Porous Media Flow Coupling (Multiphysics Coupling), and the Mixture Model multiphysics coupling.

	Please find related information under
🔍	• Theory for the Phase Transport Mixture Model Interfaces • Theory for the Free and Porous Media Flow, Darcy Interface • Theory for the Multiphase Flow in Porous Media Interface in the *CFD Module User's Guide*.

The Bubbly Flow Interface

In this section:

The Laminar Bubbly Flow Interface

The **Laminar Bubbly Flow (bf)** interface ( ), found under the **Multiphase Flow>Bubbly Flow** branch ( ) when adding a physics interface, is used to model the flow of liquids with dispersed bubbles at low and moderate Reynolds numbers.

It is assumed that the bubbles only occupy a small volume fraction and that they always travel with their terminal velocity. It is thereby possible to solve only one set of Navier–Stokes equations for the liquid phase and to let the velocity of the bubbles be guided by a slip model. The pressure distribution is computed from a mixture-averaged continuity equation. The volume fraction of bubbles is tracked by solving a transport equation for the effective gas density.

The physics interface can also model the distribution of the number density, that is, the number of bubbles per unit volume which in turn can be used to calculate the interfacial area, useful when simulating chemical reactions in the mixture.

The main physics node is the Fluid Properties feature, which adds the equations for laminar bubbly flow and provides an interface for defining the fluid materials for the liquid and the gas and the slip velocity model to use.

When this physics interface is added, the following default physics nodes are also added in the **Model Builder** — **Laminar Bubbly Flow**, **Fluid Properties**, **Wall** (the default boundary types are **No slip** for the liquid and **No gas flux** for the gas), and **Initial Values**. Then, from the **Physics** toolbar, add other nodes that implement, for example, boundary conditions and volume forces. You can also right-click **Laminar Bubbly Flow** 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 `bf`.

PHYSICAL MODEL

Specify if the gas concentration is low and whether or not to solve for the interfacial area.

Low Gas Concentration

The **Low gas concentration** check box is selected by default. This approximation is valid if the gas volume fraction is low (ϕ_g less than a few percent) and its density does not have any significant effects on the continuity equation. It is then generally valid to replace the continuity equation in The Bubbly Flow Equations.

Solve for Interfacial Area

To add a transport equation for the bubble density in order to determine the interfacial area, select the **Solve for interfacial area** check box.

Reference Values

Reference values are global quantities used to evaluate the density of the liquid and the absolute pressure p_A.

Reference pressure level   There are generally two ways to include the pressure in fluid flow computations: either to use the absolute pressure $p_A = p + p_{ref}$, or the gauge pressure p. When p_{ref} is nonzero, the physics interface solves for the gauge pressure whereas material properties are evaluated using the absolute pressure. The reference pressure level is also used to define the density of the liquid. The default **Reference pressure level** p_{ref} (SI unit: Pa) is 1 atm.

Reference temperature   The reference temperature is used to define the density of the liquid. The default **Reference temperature** T_{ref} (SI unit: K) is 293.15 K.

Swirl Flow

For 2D axisymmetric models, select the **Swirl flow** check box to include the swirl velocity component — that is, the velocity component u_φ in the azimuthal direction. While u_φ can be nonzero, there can be no gradients in the φ direction. Also see in the CFD Module User's Guide.

The dependent variables (field variables) are the **Velocity field, liquid phase u** (SI unit: m/s), the **Pressure** p (SI unit: Pa), the **Effective gas density** rhogeff (SI unit: kg/m^3), and the **Number density, gas phase** nd (SI unit: $1/m^3$). The names can be changed but the names of fields and dependent variables must be unique within a component.

CONSISTENT STABILIZATION AND INCONSISTENT STABILIZATION

To display this section, click the **Show More Options** button (�}) and select **Stabilization** in the **Show More Options** dialog box. This section contains the settings for stabilization of the momentum transport (the fluid flow) in the **Momentum transport** area and stabilization of the equation for the dispersed phase in the **Gas phase transport** area.

Consistent streamline and crosswind diffusion is applied by default to both gas and momentum transport. Additional inconsistent stabilization terms may be added when required as isotropic diffusion.

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 the **Use pseudo time stepping for stationary equation form** check box to add pseudo time derivatives to the equation when the **Stationary equation** form is used. When selected, also choose a **CFL number expression** — **Automatic** (the default) or **Manual**. **Automatic** sets the local CFL number (from the Courant–Friedrichs–Lewy condition) to the built-in variable CFLCMP which in turn triggers a PID regulator for the CFL number. For **Manual** enter a **Local CFL number** CFL_{loc} (dimensionless).

⊕	• Pseudo Time Stepping for Laminar Flow Models in this guide and Pseudo Time Stepping in the *COMSOL Multiphysics Reference Manual* • Domain and Boundary Nodes for Bubbly Flow • Theory for the Bubbly Flow Interface

Domain and Boundary Nodes for Bubbly Flow

The following domain and boundary 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. Subnodes are available by clicking the parent node and selecting it from the **Attributes** menu.

DOMAIN

- Fluid Properties
- Volume Force (described for The Laminar Flow and Creeping Flow Interfaces)
- Mass Transfer
- Gravity
- Initial Values

BOUNDARY

	The sections describe the available boundary conditions for the liquid and the gas. In all equations, **n** denotes the outward pointing unit vector normal to the boundary.

The boundary types for the liquid flow variables, described in this section, are:

- Wall (the default boundary condition)
- Inlet
- Outlet
- Symmetry
- Periodic Flow Condition
- Interior Wall

PAIR

- Flow Continuity

In addition to the boundary conditions for the liquid, the following boundary conditions for the gas are available for all boundary condition types except symmetry and interior wall:

- Gas Concentration (the default condition for inlets)
- Gas Flux
- Gas Outlet (the default condition for outlets)
- No Gas Flux (the default condition for walls)
- Symmetry

🔍	Gas Boundary Condition Equations

⬚	For 2D 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 the axial symmetry boundaries only.

Fluid Properties

The **Fluid Properties** node contains the material properties for the liquid and the gas. It also contains settings for the slip model.

MODEL INPUTS

Fluid properties, such as the gas density and liquid viscosity, can be defined through user inputs, variables, or by selecting a material. For the latter option, additional inputs, for example temperature or pressure, may be required to define these properties.

Temperature

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.

Absolute Pressure

This input appears when a material requires the absolute pressure as a model input. The absolute pressure is used to evaluate material properties, but it also relates to the value of the calculated pressure field. There are generally two ways to calculate the pressure when describing fluid flow: either to solve for the absolute pressure or for a pressure (often denoted gauge pressure) that relates to the absolute pressure through a reference pressure.

The default **Absolute pressure** p_A is $p+p_{ref}$, where p is the dependent pressure variable from the Navier–Stokes or RANS equations, and p_{ref} is from the user input defined at the physics interface level. When p_{ref} is nonzero, the physics interface solves for a gauge pressure. If the pressure field instead is an absolute pressure field, p_{ref} should be set to 0.

The **Absolute pressure** field can be edited by clicking **Make All Model Inputs Editable** (🖊) and entering the desired value in the input field.

> 🔍   Model Inputs and Multiphysics Couplings in the *COMSOL Multiphysics Reference Manual*

MATERIALS

Select the materials to use for the material properties of the liquid and the gas (when they are set to take their value from the material). The default is to use the **Domain material** for the **Liquid** and **None** for the **Gas**. Select another material to use that material's properties for the liquid or gas as needed.

LIQUID PROPERTIES

The default **Density, liquid phase** ρ_l (SI unit: kg/m^3) uses values **From material**. For **User defined** enter another value or expression.

The density in a material can depend on temperature and/or pressure and these dependencies are automatically replaced by p_{ref} and T_{ref}, which are specified at the physics interface level.

The default **Dynamic viscosity, liquid phase** μ_l (SI unit: Pa·s) uses values **From material**; the value is then defined for the material selected in the **Materials** section for the continuous phase. For **User defined** enter another value or expression.

The dynamic viscosity describes the relationship between the shear stresses and the shear rate in a fluid. Intuitively, water and air have a low viscosity, and substances often described as thick, such as oil, have a higher viscosity.

GAS PROPERTIES

The default **Density, gas phase** ρ_g (SI unit: kg/m^3) uses values **From material**. For **User defined** enter another value or expression. Alternatively, select **Calculate from ideal gas law** and enter the **Molecular weight** M (SI unit: kg/mol) of the gas.

Enter the **Bubble diameter** d_b (SI unit: m). The default value is 10^{-3} m (1 mm).

SLIP MODEL

Select a **Slip model** — **Homogeneous flow** (the default), **Pressure-drag balance**, or **User defined**.

Homogeneous flow assumes that the velocity of the two phases are equal; that is, $\mathbf{u}_{\text{slip}} = 0$. For **User defined** enter different values or expressions for the components of the **Slip velocity** $\mathbf{u}_{\text{slip}}$ (SI unit: m/s).

For **Pressure-drag balance** it uses a model based on the assumption that the pressure forces on a bubble are balanced by the drag force:

$$\frac{3}{4}\frac{C_d}{d_b}\rho_l|\mathbf{u}_{\text{slip}}|\mathbf{u}_{\text{slip}} = -\nabla p$$

Here d_b (SI unit: m) is the bubble diameter, and C_d (dimensionless) is the drag coefficient.

Select a **Drag coefficient model**:

• **Small spherical bubbles (Hadamard-Rybczynski)** for bubbles with a diameter smaller than 2 mm.

• **Large bubbles** for gas bubbles with a diameter larger than 2 mm. Then enter the **Surface tension coefficient** σ (SI unit N/m). The default is 0.07 N/m.

• **Air bubbles in tap water (Schwarz-Turner)** for air bubbles of 1–10 mm mean diameter in water.

User defined to enter a different value or expression for the **Drag coefficient** C_d (dimensionless). The default value is 1.

Mass Transfer

Add a **Mass Transfer** node to include mass transfer from the gas to the liquid.

MASS TRANSFER

Select a **Mass transfer model** — **Two-film theory**, **Nonequilibrium model**, or **User defined**. For **User defined** enter a value or expression for the **Mass transfer from gas to liquid** m_{gl} (SI unit: kg/(m^3·s)). The default is 0 kg/(m^3·s).

Nonequilibrium Model

For **Nonequilibrium model** enter values or expressions for each of the following:

- **Equilibrium volume fraction in dispersed phase** ϕ_{eq}. The default is 0.
- **Inverse time scales** f_l and f_g (SI unit: 1/s). The default is 0 s^{-1}.

The mass transfer is modeled as

$$m_{gl} = \rho_g[f_l \max(\phi_g - \phi_{eq}) - f_g \max(\phi_{eq} - \phi_g)]$$

Two-Film Theory

For **Two-film theory** enter values for the **Mass transfer coefficient** k (SI unit: m/s), **Henry's constant** H (SI unit: Pa·m^3/mol), the **Dissolved gas concentration** c (SI unit: mol/m^3), and the **Molecular weight of species** M (SI unit: kg/mol). Refer to the theory below for more information.

Henry's law gives the equilibrium concentration c^* of gas dissolved in liquid:

$$c^* = \frac{p + p_{ref}}{H}$$

where H is Henry's constant. The molar flux per interfacial area, N (SI unit: mol/(s·m^2)), is determined by

$$N = k(c^* - c)$$

where k is the Mass transfer coefficient and c is the Dissolved gas concentration in liquid.

The mass transfer from gas to liquid, m_{gl}, is given by

$$m_{gl} = NMa$$

where M is the Molecular weight of species and a is the interfacial area per volume (SI unit: m^2/m^3).

<table>
<tr><td>ⓠ</td><td>Also see Theory for the Bubbly Flow Interface for details about how a is computed.</td></tr>
</table>

For two-film theory, you also need to solve for the concentration of the dissolved gas;

$$\frac{\partial c}{\partial t} + \nabla \cdot (c\mathbf{u}_l) = \nabla \cdot (D\nabla c) + \frac{m_{gl}}{M}$$

which can be done by adding a Transport of Diluted Species interface.

Gravity

The **Gravity** node adds the force $\rho\mathbf{g}$ to the right-hand side of the momentum transport equation. Gravity nodes are mutually exclusive, that is, there can only be one active Gravity node per domain.

GRAVITY

Enter the components of the **Gravity vector**, $\mathbf{g}$ (SI unit: m/s^2). For 2D components the default Gravity vector is defined as (0, –g_const). Here g_const is a physical constant equal to 9.8066 m/s^2. For 3D and 2D axisymmetric components, the gravity acts in the negative z direction by default.

Initial Values

The **Initial Values** node adds initial values for the flow variables and the effective gas density that can serve as initial conditions for a transient simulation or as an initial guess for a nonlinear solver.

INITIAL VALUES

Enter initial values or expressions for the **Velocity field, liquid phase u** (SI unit: m/s) and for the **Pressure** p (SI unit: Pa). The default values are 0. Also enter a value or expression for the **Effective gas density** rhogeff (SI unit: kg/m^3). The default is 0 kg/m^3.

If the **Solve for interfacial area** check box is selected, enter an initial value for the **Number density, gas phase** nd (SI unit: $1/m^3$). The default is 0 $1/m^3$.

Wall

The **Wall** node adds a selection of boundary conditions that describe the existence of a solid wall. The Wall node by default specifies no gas flux for the gas phase.

⊚	Gas Boundary Condition Equations

LIQUID BOUNDARY CONDITION

Select a **Liquid boundary condition** — **No slip** (the default) or **Slip**.

No Slip
No slip is the default boundary condition for the liquid. A no slip wall is a wall where the liquid velocity relative to the wall velocity is zero. For stationary walls, it sets the liquid velocity to zero at the wall:

$$\mathbf{u}_l = 0$$

Slip
Sets the velocity component normal to the wall to zero:

$$\mathbf{u}_l \cdot \mathbf{n} = 0$$

GAS BOUNDARY CONDITION

From the list, select a **Gas boundary condition** for the gas phase on the wall — **No gas flux** (the default), **Gas concentration**, **Gas outlet**, **Gas flux**, or **Symmetry**.

Gas Concentration
For **Gas concentration** enter the **Effective gas density** $\rho_g \phi_{g0}$ (SI unit: kg/m^3). The default is 0 kg/m^3. If **Solve for interfacial area** is selected, also select either the **Bubble number density** (the default) or the **Bubble diameter and gas density** button.

- For **Bubble number density** enter the **Bubble number density** n_0 (SI unit: 1/m^3). The default is 1000 1/m^3.

- For **Bubble diameter and gas density** enter the **Bubble diameter** d_b (SI unit: m) (the default is 1 mm) and **Density, gas phase** ρ_g (SI unit: kg/m^3) (the default is 1 kg/m^3).

Gas Flux

For **Gas flux** enter the **Gas mass flux** $N_{\rho_g \phi_g}$ (SI unit: kg/(m^2·s)) (the default is 0 kg/(m^2·s)) and if the **Solve for interfacial area** check box is selected on the physics interface, the **Number density flux** N_n (SI unit: 1/(m^2·s)). The default is 0 (1/(m^2·s)).

WALL MOVEMENT

This section contains controls to describe the wall movement relative to the spatial frame.

The **Translational velocity** setting controls the translational velocity, $\mathbf{u}_{tr}$. The list is per default set to **Automatic from frame**. When **Automatic from frame** is selected, the physics automatically detects if the spatial frame moves. If there is no movement, $\mathbf{u}_{tr}$ is set to **0**. If the frame moves, $\mathbf{u}_{tr}$ becomes equal to the frame movement. $\mathbf{u}_{tr}$ is accounted for in the actual boundary condition prescribed in the **Liquid boundary condition** section.

When **Manual** is selected from **Translational velocity** selection list, the **Velocity of moving wall**, $\mathbf{u}_{tr}$ can be prescribed manually. Specifying the translational velocity manually does not automatically cause the associated wall to move. An additional Moving Mesh interface needs to be added to physically track the wall movement in the spatial reference frame.

The **Sliding wall** option is appropriate if the surface is sliding in its tangential direction. A velocity is prescribed at the wall and the boundary itself does not have to actually move relative to the reference frame.

CONSTRAINT SETTINGS

This section is displayed by clicking the **Show More Options** button (👁) and selecting **Advanced Physics Options.**

🔍	Wall in the Single-Phase Flow interfaces

Inlet

The **Inlet** node adds a selection of boundary conditions that describe inlets in fluid-flow simulations.

🔍	Gas Boundary Condition Equations

LIQUID BOUNDARY CONDITION

Select a **Liquid boundary condition** — **Velocity** (the default), **Pressure**, or **Fully developed flow**.

VELOCITY

For **Velocity** click the **Normal inflow velocity** (the default) or **Velocity field** buttons.

- For **Normal inflow velocity** enter a value or expression for U_0 (SI unit: m/s).

- For **Velocity field** specify that the velocity at the boundary is equal to a given $\mathbf{u}_0$ (SI unit: m/s) and enter the components in the matrix:

$$\mathbf{u}_l = \mathbf{u}_0$$

PRESSURE

This condition specifies the normal stress which in most cases is approximately equal to the pressure. Enter the **Pressure** p_0 (SI unit: Pa) at the boundary. The default is 0 Pa. Enter a relative pressure value in p_0 (SI unit: Pa). Or if the reference pressure p_{ref} defined at the physics interface level is equal to 0 Pa, enter an absolute pressure in p_0.

- The **Suppress backflow** check box is selected by default. This option adjusts the inlet pressure, $\hat{p}_0 \geq p_0$, locally in order to reduce the amount of fluid exiting the domain through the boundary. If suppress backflow is deselected, the inlet boundary can become an outlet depending on the pressure field in the rest of the domain.

- **Flow direction** controls in which direction the fluid enters the domain.

  - For **Normal flow** (the default) it prescribes zero tangential velocity component.

  - For **User defined** define an **Inflow velocity direction**, $\mathbf{d_u}$ (dimensionless). The magnitude of $\mathbf{d_u}$ does not matter, only the direction. $\mathbf{d_u}$ must point into the domain.

FULLY DEVELOPED FLOW

The **Fully developed flow** option adds contributions to the inflow boundary, which force the flow toward the solution for a fully developed channel flow. The channel can be thought of as a virtual extrusion of the inlet cross section. The velocity is defined by the boundary condition of the adjacent boundary in the model.

The boundary conditions for the virtual inlet channel are inherited from the boundaries adjacent to the inlet channel. Virtual boundaries adjacent to walls (except slip walls) are treated as no-slip walls. Virtual boundaries adjacent to any other type of boundary are treated as slip-walls (or equivalently as symmetry boundaries).

Select a **Fully developed flow** option — **Average velocity** (the default), **Flow rate**, or **Average pressure**.

The **Fully developed flow** option adds contributions to the inflow boundary, which force the flow toward the solution for a fully developed channel flow.

Select an option to control the flow rate at the inlet:

- For **Average velocity** enter U_{av}.
- **Flow rate**, V_0. Two-dimensional models also require an **Entrance thickness**, D_z, which is the out-of-plane thickness of the extruded entrance channel.
- **Average pressure**, P_{av}. Observe that P_{av} is the average pressure on the inflow boundary.

Fully developed inflow can be used in conjunction with the turbulence models. No additional inputs are required for the turbulence variables. They are instead solved for on the inlet boundary to be consistent with the fully developed flow profile.

A fully developed flow boundary cannot be adjacent to any Interior Wall feature

GAS BOUNDARY CONDITION

These settings are the same as for Wall. See Gas Boundary Condition. The only difference is that **Gas concentration** is the default.

Outlet

The **Outlet** node adds a set of boundary conditions that describe outlets in fluid-flow simulations; that is, the conditions at boundaries where the fluid exits the domain.

LIQUID BOUNDARY CONDITION

Select a **Liquid boundary condition** — **Pressure** (the default), **Velocity**, or **Fully developed flow**.

PRESSURE CONDITIONS

The **Pressure** condition specifies the normal stress which in most cases is approximately equal to the pressure. The tangential stress component is set to $0 \ \text{N/m}^2$.

- Enter the **Pressure** p_0 (SI unit: Pa) at the boundary. The default is 0 Pa. Enter a relative pressure value in p_0 (SI unit: Pa). Or if the reference pressure p_{ref} defined at the physics interface level is equal to 0 Pa, enter an absolute pressure in p_0.

- Select the **Normal flow** check box to change the no tangential stress condition to a no tangential velocity condition. This forces the flow to exit (or enter) the domain perpendicularly to the outlet boundary.

- The **Suppress backflow** check box is selected by default. This option adjusts the outlet pressure in order to reduce the amount of fluid entering the domain through the boundary.

VELOCITY

For **Velocity** click the **Velocity field** (the default) or **Normal outflow velocity** buttons.

- For **Velocity field** specify that the velocity at the boundary is equal to a given $\mathbf{u}_0$ (SI unit: m/s) and enter the components in the matrix:

$$\mathbf{u}_l = \mathbf{u}_0$$

- For **Normal outflow velocity** enter a value or expression for U_0 (SI unit: m/s).

FULLY DEVELOPED FLOW

This boundary condition is applicable when the flow exits the domain into a long pipe or channel, at the end of which a flow profile is fully developed.

The boundary conditions for the virtual inlet channel are inherited from the boundaries adjacent to the outlet channel. Virtual boundaries adjacent to walls (except slip walls) are treated as no-slip walls. Virtual boundaries adjacent to any other type of boundary are treated as slip-walls (or equivalently as symmetry boundaries).

Select a **Fully developed flow option** — **Average velocity** (the default), **Flow rate**, or **Average pressure**.

The settings for the **Gas boundary condition** are the same as for Wall. See Gas Boundary Condition.

When the **Gas boundary condition** is set to **Gas outlet**, the **Exterior gas condition(s)** section contains an input field for the **Effective gas density** on the downstream side of the outlet. If **Solve for interfacial area** is selected at the physics interface level, additional input fields appear for the **Bubble number density** or the **Bubble diameter and gas density** on the downstream side of the outlet.

	See in the Single-Phase Flow interfaces

Symmetry

The **Symmetry** node adds boundary conditions that describe symmetry boundaries in fluid-flow simulations. The boundary condition for symmetry boundaries prescribes no penetration and vanishing shear stresses:

$$\mathbf{u}_1 \cdot \mathbf{n} = 0, \qquad \mathbf{t}^T\left(\phi_1(\mu_1 + \mu_T)\left(\nabla\mathbf{u}_1 + \nabla\mathbf{u}_1^T - \frac{2}{3}(\nabla \cdot \mathbf{u}_1)\mathbf{I}\right)\right)\mathbf{n} = 0$$

BOUNDARY SELECTION

A boundary condition for 2D axial symmetry is not required.

For the symmetry axis at $r = 0$, the software automatically provides a condition that prescribes $u_r = 0$ and vanishing stresses in the z direction and adds an **Axial Symmetry** node that is valid on the axial symmetry boundaries only.

Periodic Flow Condition

The **Periodic Flow Condition** splits its selection into a source group and a destination group. Fluid that leaves the domain through one of the destination boundaries enters the domain through the corresponding source boundary. This corresponds to a situation where the geometry is a periodic part of a larger geometry. If the boundaries are not parallel to each other, the velocity vector is automatically transformed.

If the boundaries are curved, the orientation of the source must be specified manually (see).

PRESSURE DIFFERENCE

A value or expression should be specified for the **Pressure difference**, $p_{\mathrm{src}} - p_{\mathrm{dst}}$. This pressure difference can, for example, drive the fully developed flow in a channel.

To set up a periodic boundary condition, both boundaries must be selected in the **Periodic Flow Condition** node. COMSOL Multiphysics automatically assigns one boundary as the source and the other as the destination. To manually set the destination selection, a **Destination Selection** section is available when the **Manual Destination Selection** option is selected in the context menu for the **Periodic Flow Condition** node.

CONSTRAINT SETTINGS

This section is displayed by clicking the **Show More Options** button (☞) and selecting **Advanced Physics Options** in the **Show More Options** dialog box.

ORIENTATION OF SOURCE

To display this section, click the **Show More Options** button (☞) and select **Advanced Physics Options** in the **Show More Options** dialog box. For information about the **Orientation of Source** section, see Orientation of Source and Destination in the *COMSOL Multiphysics Reference Manual*.

ORIENTATION OF DESTINATION

This section appears if the setting for **Transform to intermediate map** in the **Orientation of Source** section is changed from the default value, **Automatic**, and **Advanced Physics Options** is selected in the **Show More Options** dialog box. For information about the **Orientation of Destination** section, see Orientation of Source and Destination in the *COMSOL Multiphysics Reference Manual*.

Interior Wall

The **Interior Wall** node adds a wall boundary condition on interior boundaries. It is similar to the Wall boundary condition available on exterior boundaries except that it applies on both sides of an interior boundary. It allows discontinuities of the dependent variables across the boundary. The Interior Wall node specifies no gas flux for the gas phase.

ℚ	Gas Boundary Condition Equations

LIQUID BOUNDARY CONDITION

Select a **Liquid boundary condition** — **No slip** (the default) or **Slip**.

No Slip

No slip is the default boundary condition for the liquid. A no slip wall is a wall where the liquid velocity relative to the wall velocity is zero. For interior stationary walls, it sets the liquid velocity to zero on both sides of the wall:

$$\mathbf{u}_l = 0$$

For turbulent bubbly flows, the no slip condition may either be prescribed exactly or modeled using automatic wall treatment or wall functions depending on the **Wall Treatment** setting in the **Turbulence** section of the interface settings.

Slip

The **Slip** condition prescribes a no-penetration condition. For an interior stationary wall it sets the velocity component normal to the interior wall to zero on both sides of the wall:

$$\mathbf{u}_l \cdot \mathbf{n} = 0$$

WALL MOVEMENT

This section contains controls to describe the wall movement relative to the spatial frame.

The **Translational velocity** setting controls the translational velocity, $\mathbf{u}_{tr}$. The list is per default set to **Automatic from frame**. When **Automatic from frame** is selected, the physics automatically detects if the spatial frame moves. If there is no movement, $\mathbf{u}_{tr}$ is set to **0**. If the frame moves, $\mathbf{u}_{tr}$ becomes equal to the frame movement. $\mathbf{u}_{tr}$ is accounted for in the actual boundary condition prescribed in the **Liquid boundary condition** section.

When **Manual** is selected from **Translational velocity** selection list, the **Velocity of moving wall**, $\mathbf{u}_{tr}$ can be prescribed manually. Specifying the translational velocity manually does not automatically cause the associated wall to move. An additional Moving Mesh interface needs to be added to physically track the wall movement in the spatial reference frame.

This section is displayed by clicking the **Show More Options** button (☞) and selecting **Advanced Physics Options.**

⊚	Wall

Flow Continuity

The **Flow Continuity** condition is suitable for pairs where the boundaries match; it prescribes that the flow field is continuous across the pair.

The parts of the boundary where a source boundary lacks a corresponding destination boundary and vice versa will get conditions from other boundary conditions under the physics interface acting as fallback boundary conditions on the nonoverlapping parts. By default, the Wall node is used as fallback unless another feature has been selected for the boundary.

⊚	About Identity and Contact Pairs

Gas Boundary Condition Equations

In addition to the boundary conditions for the liquid, specify boundary conditions for the gas on Wall, Inlet, Outlet, and Interior Wall nodes. Select a **Gas Boundary Condition**:

Gas Concentration
Using this boundary condition, specify the effective gas density.

$$\tilde{\rho}_g = \tilde{\rho}_g^{\,0}$$

Gas Outlet
This boundary condition is appropriate for boundaries where the gas phase flows outward with the gas velocity, $\mathbf{u}_g$, at the boundary.

Gas Flux
Using this boundary condition, specify the gas mass flux through the boundary:

$$-\mathbf{n} \cdot (\tilde{\rho}_g \mathbf{u}_g) = N_{\rho_g \phi_g}$$

Symmetry

This boundary condition, which is useful on boundaries that represent a symmetry line for the gas flow, sets the gas flux through the boundary to zero:

$$\mathbf{n} \cdot (\tilde{\rho}_g \mathbf{u}_g) = 0$$

No Gas Flux

This boundary condition represents boundaries where the gas flux through the boundary is zero:

$$\mathbf{n} \cdot (\phi_g \mathbf{u}_g) = 0$$

In walls moving with a boundary velocity $\mathbf{u}_{bnd}$, the gas flux through the boundary is:

$$\mathbf{n} \cdot (\phi_g \mathbf{u}_g) = \mathbf{n} \cdot (\phi_g \mathbf{u}_{bnd})$$

The Mixture Model Interface

In this section:

The Mixture Model, Laminar Flow Interface

The **Mixture Model, Laminar Flow (mm)** interface ( ), found under the **Multiphase Flow>Mixture Model** branch ( ) when adding a physics interface, is used to model the flow at low and moderate Reynolds numbers of liquids containing a dispersed phase. The dispersed phase can be bubbles, liquid droplets, or solid particles, which are assumed to always travel with their terminal velocity.

The Mixture Model, Laminar Flow interface solves one set of Navier–Stokes equations for the momentum of the mixture. The pressure distribution is calculated from a mixture-averaged continuity equation and the velocity of the dispersed phase is described by a slip model. The volume fraction of the dispersed phase is tracked by solving a transport equation for the volume fraction.

The physics interface can also model the distribution of the number density, which in turn can be used to calculate the interfacial area, which is useful when simulating chemical reactions in the mixture.

The main physics node is the Mixture Properties feature. It adds the equations for the mixture and provides an interface for defining the fluid materials for the continuous and dispersed phases as well as which slip model and mixture viscosity model to use.

When this physics interface is added, the following default physics nodes are also added in the **Model Builder** — **Mixture Properties**, **Wall**, and **Initial Values**. Then, from the **Physics** toolbar, add other nodes that implement, for example, boundary conditions and volume forces. You can also right-click **Mixture Model, Laminar Flow** 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 `mm`.

PHYSICAL MODEL

Specify the characteristics of the dispersed phase, the model for the slip velocity, and whether or not to solve for the interfacial area.

Dispersed Phase

To characterize the **Dispersed phase**, select **Solid particles** (the default) or **Liquid droplets/bubbles**.

The selection from this list is further defined for the Mixture Properties node under the Mixture Model section.

Slip Model

To compute the slip velocity $\mathbf{j}_{\text{slip}}$ (SI unit: m/s), select a **Slip model** — **Homogeneous flow** (the default), **Hadamard-Rybczynski**, **Schiller-Naumann**, **Haider-Levenspiel**, or **User defined**.

- The **Homogeneous flow** model assumes that the velocities of the two phases are equal, that is, $\mathbf{u}_{\text{slip}} = 0$.

- In most cases there is a significant difference in the velocity fields due to the buoyancy of the dispersed phase. Use one of the predefined slip models for such cases.

- For **User defined** specify an arbitrary expression for the relative velocity. For example, give a constant velocity based on experimental data. Enter the **Slip velocity field $\mathbf{u}_{\text{slip}}$** (SI unit: m/s) or **Slip flux $\mathbf{j}_{\text{slip}}$** (SI unit: m/s) in the Mixture Properties node under the Mixture Model section.

Solve For Interfacial Area

To add a transport equation for the number density of the dispersed particles, in order to determine the interfacial area, select the **Solve for interfacial area** check box (by default not selected).

For the Mass Transfer rate, use a two-film theory model, which includes the interfacial area per unit volume between the two phases. It is possible to compute the interfacial area per unit volume if the number density n (that is, the number of dispersed particles

per volume) is known. Select the **Solve for interfacial area** check box to add the following equation for the number density n:

$$\frac{\partial n}{\partial t} + \mathbf{j} \cdot \nabla n + \nabla \cdot (n \mathbf{u}_{slip} \phi_c) = 0$$

This equation states that a dispersed phase particle cannot disappear, appear, or merge with other particles, although it can expand or shrink.

The Mixture Model, Laminar Flow Interface calculates the interfacial area a (SI unit: m^2/m^3) from

$$a = (4 n \pi)^{1/3} (3 \phi_d)^{2/3}$$

Reference values
Reference values are global quantities used to evaluate the density of both phases and the absolute pressure p_A.

Reference pressure level There are generally two ways to include the pressure in fluid flow computations: either to use the absolute pressure $p_A = p + p_{ref}$, or the gauge pressure p. When p_{ref} is nonzero, the physics interface solves for the gauge pressure whereas material properties are evaluated using the absolute pressure. The reference pressure level is also used to define the density of both phases. The default **Reference pressure level** p_{ref} (SI unit: Pa) is 1[atm].

Reference temperature The reference temperature is used to define the density of both phases. The default **Reference temperature** T_{ref} (SI unit: K) is 293.15[K].

Swirl Flow
For 2D axisymmetric components, select the **Swirl flow** check box to include the swirl velocity component — that is, the velocity component j_φ in the azimuthal direction. While j_φ can be nonzero, there can be no gradients in the φ direction.

| 🔍 | General Single-Phase Flow Theory |

DEPENDENT VARIABLES
Enter values for the dependent variables (field variables):

- **Velocity field, mixture j** (SI unit: m/s)

- **Pressure** p (SI unit: Pa)
- **Volume fraction, dispersed phase** phid (dimensionless)
- **Squared slip velocity** slipvel
- **Number density, dispersed phase** nd (SI unit: $1/m^3$).

The names can be changed but the names of fields and dependent variables must be unique within a component.

CONSISTENT STABILIZATION AND INCONSISTENT STABILIZATION

To display this section, click the **Show More Options** button (👁) and select **Stabilization** in the **Show More Options** dialog box.

The consistent stabilizations **Streamline diffusion** and **Crosswind diffusion** are by default applied to the **Navier-Stokes and dispersed phase transport equations**. In addition, when the flow is turbulent, the consistent stabilizations are also applied to the **Turbulence**. Additional inconsistent stabilization terms may be added when required as isotropic diffusion.

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.

Penalty Diffusion can be used to suppress negative values of the dispersed volume fraction. Including this term has been observed to slow down convergence and it is therefore disabled by default.

Select the **Use pseudo time stepping for stationary equation form** check box to add pseudo time derivatives to the equation when the **Stationary equation** form is used. When selected, also choose a **CFL number expression** — **Automatic** (the default) or **Manual**. **Automatic** sets the local CFL number (from the Courant–Friedrichs–Lewy condition) to the built-in variable CFLCMP which in turn triggers a PID regulator for the CFL number. For **Manual** enter a **Local CFL number** CFL_{loc} (dimensionless).

🔍	• Pseudo Time Stepping for Laminar Flow Models in this guide and Pseudo Time Stepping in the *COMSOL Multiphysics Reference Manual* • Domain and Boundary Nodes for the Mixture Model Interface • Slip Velocity Models and Theory for the Mixture Model Interface

	Polymer Electrolyte Membrane Electrolyzer: Application Library path **Fuel_Cell_and_Electrolyzer_Module/Electrolyzers/pem_electrolyzer**

Domain and Boundary Nodes for the Mixture Model Interface

The following domain and boundary 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. Subnodes are available by clicking the parent node and selecting it from the **Attributes** menu.

DOMAIN

- Mixture Properties
- Mass Transfer
- Volume Force (described for The Laminar Flow Interface)
- Gravity
- Initial Values

BOUNDARY

The boundary types for the mixture flow variables, described in this section, are:

- Wall (the default boundary condition feature)
- Inlet
- Outlet
- Symmetry
- Periodic Flow Condition
- Interior Wall

PAIR

- Mixture Continuity

For the flow variables, the velocity and the pressure, the boundary conditions correspond to those defined for single phase flow (see). There is also a point constraint

for the pressure, which is useful if no other boundary condition in the model includes a pressure level constraint.

The following boundary conditions for the dispersed phase are available for all boundary condition types except symmetry and interior wall. These are described in more detail in the .

- **Dispersed phase concentration** (the default condition for inlets)
- **Dispersed phase flux**
- **Dispersed phase outlet** (the default condition for outlets)
- **No dispersed phase flux** (the default condition for walls)
- **Symmetry**

	For 2D 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.

Mixture Properties

The **Mixture Properties** node contains the material properties for the continuous phase and the dispersed phase. It also contains settings for the viscosity model. For the Mixture Model, Turbulent Flow interfaces, the **Mixture Properties** node also adds the equations for the turbulence transport equations.

MODEL INPUTS

The viscosity of each phase can be defined through user inputs, variables, or by selecting a material. For the latter option, additional inputs, for example temperature or pressure, may be required to define these properties.

Temperature

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.

Absolute Pressure
This input appears when a material requires the absolute pressure as a model input. The absolute pressure is used to evaluate material properties, but it also relates to the value of the calculated pressure field. There are generally two ways to calculate the pressure when describing fluid flow: either to solve for the absolute pressure or for a pressure (often denoted gauge pressure) that relates to the absolute pressure through a reference pressure.

The default **Absolute pressure** p_A is $p + p_{ref}$, where p is the dependent pressure variable from the Navier–Stokes or RANS equations, and p_{ref} is from the user input defined at the physics interface level. When p_{ref} is nonzero, the physics interface solves for a gauge pressure. If the pressure field instead is an absolute pressure field, p_{ref} should be set to 0.

The **Absolute pressure** field can be edited by clicking **Make All Model Inputs Editable** ( ) and entering the desired value in the input field.

Ⓠ Model Inputs and Multiphysics Couplings in the *COMSOL Multiphysics Reference Manual*

MATERIALS
Select the fluid materials to use for the material properties. The default material used for the **Continuous phase** is the **Domain material**. This corresponds to the material currently applied to the domain in question. The **Dispersed phase** uses **None** per default. A valid material must be selected instead.

CONTINUOUS PHASE PROPERTIES
The default **Density, continuous phase** ρ_c (SI unit: kg/m^3) uses values **From material** (as selected in the **Materials** section). For **User defined** enter another value or expression. In this case the default is 0 kg/m^3.

The density in a material can depend on temperature and/or pressure and these dependencies are automatically replaced by p_{ref} and T_{ref}, which are specified at the physics interface level.

The default **Dynamic viscosity, continuous phase** μ_c (SI unit: Pa·s), uses values **From material**. It describes the relationship between the shear stresses and the shear rate in a

fluid. Intuitively, water and air have a low viscosity, and substances often described as thick, such as oil, have a higher viscosity. For **User defined** enter another value or expression. In this case, the default is 0 Pa·s.

DISPERSED PHASE PROPERTIES

The default **Density, dispersed phase** ρ_d (SI unit: kg/m^3) uses values **From material** (as selected in the **Materials** section). For **User defined** enter another value or expression. In this case, the default is 0 kg/m^3.

The density in a material can depend on temperature and/or pressure and these dependencies are automatically replaced by p_{ref} and T_{ref}, which are specified at the physics interface level.

Enter the **Diameter of particles/droplets** d_d (SI unit: m). The default is 10^{-3} m (1 mm). If **Haider-Levenspiel** is selected for the **Slip model** under **Physical Model**, enter a value between 0 and 1 for the **Sphericity** (dimensionless). The default is 1.

If **Liquid droplets/bubbles** is selected from the **Dispersed phase** list in the interface, then **Dynamic viscosity, dispersed phase** μ_d (SI unit: Pa·s) is also available. The default uses values **From material** (as selected in the **Materials** section) or select **User defined** to enter another value or expression. In this case, the default is 0 Pa·s.

MIXTURE MODEL

The options in this section are based on the selection made from the **Dispersed phase** list for the Mixture Model interfaces.

Slip Velocity Field

When a **User defined Slip model** is selected for the physics interface, specify an arbitrary expression for the relative velocity. For example, give a constant velocity based on experimental data.

- When **Slip velocity** is set to **Specify slip velocity field**, enter the slip velocity between the two phases, $\mathbf{u}_{slip}$ (SI unit: m/s).

- When **Slip velocity** is set to **Specify slip flux**, enter the slip flux $\mathbf{j}_{slip}$ (SI unit: m/s).

🔍	• The Mixture Model Equations in Theory for the Mixture Model Interface

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Mixture Viscosity Model

Select the **Mixture viscosity model**.

- When **Solid particles** is the **Dispersed phase**, select either **Krieger type** (the default) or **User defined**.

- When **Liquid droplets/bubbles** is the **Dispersed phase**, select **Krieger type** (the default), **User defined**, or **Volume averaged**.

For **User defined** enter a value or expression for the **Dynamic viscosity** μ (SI unit: Pa·s). The default is 0 Pa·s. When using this option, make sure to limit the viscosity to bounded positive values.

When **Krieger type** is selected, enter a value or expression for the **Maximum packing concentration** ϕ_{max} (dimensionless). The default is 0.62.

Select Krieger type to model the most generally valid expression for the mixture viscosity:

$$\mu \;=\; \mu_c \left(1 - \frac{\phi_d}{\phi_{max}}\right)^{-2.5\phi_{max}\mu^*}$$

where ϕ_{max} is the maximum packing concentration, which for solid particles is approximately 0.62. The dimensionless parameter $\mu^* = 1$ for solid particles and

$$\mu^* \;=\; \frac{\mu_d + 0.4\mu_c}{\mu_d + \mu_c}$$

for droplets and bubbles. When applying the Krieger type viscosity model, ϕ_d is replaced by $\min(\phi_d, 0.999\phi_{max})$ for better robustness.

Select **Volume averaged** to model the mixture viscosity of liquid-liquid mixtures, which uses the following equation for the viscosity:

$$\mu \;=\; \phi_d\mu_d + \phi_c\mu_c$$

The Mixture Model interfaces always employ the mixture viscosity in the particle Reynolds number expression used to calculate the slip velocity, thereby accounting for the increase in viscous drag due to particle-particle interactions.

Mass Transfer

Use the **Mass Transfer** node to include mass transfer from the dispersed phase to the continuous phase.

MASS TRANSFER

Select a **Mass transfer model** — **User defined** (the default), **Nonequilibrium model**, or **Two-film theory**. For **User defined** enter a value or expression for the **Mass transfer from dispersed to continuous phase** m_{dc} (SI unit: kg/(m^3·s)). The default is 0 kg/(m^3·s).

Nonequilibrium Model

For **Nonequilibrium model** enter values or expressions for each of the following:

- **Equilibrium volume fraction in dispersed phase** ϕ_{eq}. The default is 0.
- **Inverse time scales** f_c and f_d (SI unit: 1/s). The default is 0 s^{-1}.

The mass transfer is modeled as

$$m_{dc} = \rho_d[\max(f_c(\phi_d - \phi_{eq}), 0) - \max(f_d(\phi_{eq} - \phi_d), 0)]$$

Two-Film Theory

For **Two-film theory** enter values or expressions for each of the following:

- **Mass transfer coefficient** k (SI unit: m/s). The default is 0 m/s.
- **Species concentration in dispersed phase** c_d (SI unit: mol/m^3). The default is 0 mol/m^3.
- **Species concentration in continuous phase** c_c (SI unit: mol/m^3). The default is 0 mol/m^3.
- **Molecular weight of species** M (SI unit: kg/mol). The default is 0 kg/mol.

The mass transfer is modeled as

$$m_{dc} = k(c_d - c_c)Ma$$

where k denotes the mass transfer rate, and c_d and c_c are the species concentrations in the dispersed and the continuous phase, respectively. M is the species' molecular weight, and a is the interfacial area per unit volume between the two phases. The **Mass transfer model** — **Two-film theory** is available when the **Solve for interfacial area** check box is selected (under the **Physical Model** section).

Gravity

The **Gravity** node adds the force $\rho\mathbf{g}$ to the right-hand side of the momentum transport equation.

Enter the components of the **Gravity vector**, **g** (SI unit: m/s^2). The default value is (0,-g_const) where g_const is a physical constant equal to 9.8066 m/s^2.

🝱	For 2D components, gravity acts in the negative *y* direction by default. For example, in a 2D component, the *y*-component is -g_const and the other component is 0. In this setting, g_const is a predefined physical constant for the standard gravity (acceleration due to gravity at sea level).

🝱 🝱	For 3D and 2D axisymmetric components, gravity acts in the negative *z* direction by default. For example, in a 3D component, the *z*-component is -g_const and the other components are 0. In this setting, g_const is a predefined physical constant for the standard gravity (acceleration due to gravity at sea level).

Initial Values

The **Initial Values** node adds initial values for the mixture velocity, pressure, and volume fraction of the dispersed phase, that can serve as an initial condition for a transient simulation or as an initial guess for a nonlinear solver.

INITIAL VALUES

Enter values or expressions for the following dependent variables:

- **Velocity field, mixture**, the components of **j** (SI unit: m/s). The defaults are 0 m/s.
- **Pressure** p (SI unit: Pa). The default is 0 Pa.
- **Volume fraction, dispersed phase** (dimensionless). The default is 0.
- If the **Solve for interfacial area** check box is selected for the physics interface, enter an initial value for the **Number density, dispersed phase** nd (SI unit: $1/m^3$). The default is 0 $1/m^3$.
- If a **Schiller-Naumann** or a **Haider-Levenspiel** slip model is used in the physics interface, enter an initial value for the **Squared slip velocity** slipvel (SI unit: m^2/s^2). The default is 0.081 m^2/s^2.

For the Mixture Model, Turbulent Flow interfaces, initial values for the turbulence variables should be also specified. Additional initial values may be required for:

- **Turbulent kinetic energy** k

- **Turbulent dissipation rate** ep
- **Reciprocal wall distance** G
- **Specific dissipation rate** om
- **Undamped turbulent kinematic viscosity** υ_0
- **Wall distance in viscous units** yPlus
- **Tangential velocity in viscous units** uPlus
- **Turbulent relative fluctuations** zeta
- **Elliptic blending function** alpha

!	The following sections describe the available boundary conditions for the mixture and the dispersed phase volume fraction. In all equations, **n** denotes the outward pointing unit vector normal to the boundary.

Wall

The **Wall** node has boundary conditions available that describe the existence of a solid wall.

MIXTURE BOUNDARY CONDITION

Select a **Mixture boundary condition** for the wall.

- No Slip
- Slip
- Navier Slip

No Slip
No slip is the default boundary condition for the liquid. A no slip wall is a wall where the mixture velocity relative to the wall velocity is zero. For stationary walls, it sets the mixture velocity to zero at the wall:

$$\mathbf{j} = 0$$

Slip
Select **Slip** to set the velocity component normal to the wall to zero $\mathbf{j} \cdot \mathbf{n}_{\text{wall}} = 0$.

Navier Slip

This boundary condition enforces no-penetration at the wall, $\mathbf{j} \cdot \mathbf{n}_{\text{wall}} = 0$, and adds a friction force of the form

$$\mathbf{F}_{\text{fr}} = -\frac{\mu}{\beta}\mathbf{j}_{\text{tang}}$$

where β is a slip length, and $\mathbf{j}_{\text{tang}} = \mathbf{j} - (\mathbf{j} \cdot \mathbf{n}_{\text{wall}})\mathbf{n}_{\text{wall}}$ is the velocity tangential to the wall. The boundary condition does not set the tangential velocity component to zero; however, the extrapolated tangential velocity component is 0 at a distance β outside of the wall. In cases where the wall movement is nonzero, select the **Account for the translational wall velocity in the friction force** check box to use $\mathbf{j} - \mathbf{u}_{\text{bnd}} - ((\mathbf{j} - \mathbf{u}_{\text{bnd}}) \cdot \mathbf{n}_{\text{wall}})\mathbf{n}_{\text{wall}}$ instead of $\mathbf{j}_{\text{tang}}$ in the friction force. Then, the extrapolated tangential velocity component is $\mathbf{u}_{\text{bnd}}$ at a distance β outside of the wall. Note that the **Velocity of sliding wall** $\mathbf{u}_{\text{w}}$ is always accounted for in the friction force.

The Navier Slip boundary condition is suitable for walls adjacent to a free surface when solving for laminar flow. Applying this boundary condition, the contact line (fluid-fluid-solid interface) is free to move along the wall. Note that in problems with contact lines, the tangential velocity of the wall typically represents the movement of the contact line but the physical wall is not moving. In such cases, **Account for the translational wall velocity in the friction force** should not be selected.

The **Slip length** setting is per default set to **Factor of minimum element length**. The slip length β is then defined as $\beta = f_{\text{h}}h_{\text{min}}$, where h_{min} is the smallest element side (corresponds to the element size in the wall normal direction for boundary layer elements) and f_{h} is a user input. Select **User defined** from the **Slip length** list to manually prescribe β.

DISPERSED PHASE BOUNDARY CONDITION

Select a **Dispersed phase boundary condition** — **No dispersed phase flux** (the default), **Dispersed phase concentration**, **Dispersed phase outlet**, **Dispersed phase flux**, or **Symmetry**.

- For **Dispersed phase concentration** enter a **Dispersed phase volume fraction** ϕ_{d0} (dimensionless). The default is 0. When **Solve for interfacial area** is selected under the **Physical Model** section, click either the **Dispersed phase number density** n_0 (SI unit: $1/\text{m}^3$) or **Diameter of particles/droplets** d_{d} (SI unit: m) button and enter a value or expression for n_0 (the default is $5 \cdot 10^6 \ 1/\text{m}^3$) or d_{d} (the default is 1 mm).

- For **Dispersed phase flux** enter values or expression for the **Dispersed phase flux** $N_{\phi\text{d}}$ (SI unit: m/s) and, if **Solve for interfacial area** is selected under the **Physical Model**

section, the **Number density flux** N_n (SI unit: $1/(m^2 \cdot s)$). The defaults are 0 m/s and 0 $1/(m^2 \cdot s)$, respectively.

Q	Dispersed Phase Boundary Condition Equations

WALL MOVEMENT

This section contains controls to describe the wall movement relative to the lab (or spatial) frame.

The **Translational velocity** setting controls the translational wall velocity, $\mathbf{u_{tr}}$. The list is per default set to **Automatic from frame**. The physics automatically detects if the spatial frame moves. This can for example happen if an ALE interface is present in the model component. If there is no movement $\mathbf{u_{tr}} = \mathbf{0}$. If the frame moves, $\mathbf{u_{tr}}$ becomes equal to the frame movement. $\mathbf{u_{tr}}$ is accounted for in the actual boundary condition prescribed in the **Boundary condition** section.

Select **Manual** from **Translational velocity** selection list in order to manually prescribe **Velocity of moving wall**, $\mathbf{u_{tr}}$. This can for example be used to model an oscillating wall where the magnitude of the oscillations are very small compared to the rest of the model. Specifying translational velocity manually does not automatically cause the associated wall to move. An additional Moving Mesh interface needs to be added to physically track the wall movement in the spatial reference frame.

The **Sliding wall** option is appropriate if the wall behaves like a conveyor belt; that is, the surface is sliding in its tangential direction. A velocity is prescribed at the wall and the boundary itself does not have to actually move relative to the reference frame.

- For 3D components, values or expressions for the **Velocity of sliding wall** $\mathbf{u_w}$ should be specified. If the velocity vector entered is not in the plane of the wall, COMSOL Multiphysics projects it onto the tangential direction. Its magnitude is adjusted to be the same as the magnitude of the vector entered.

- For 2D components, the tangential direction is unambiguously defined by the direction of the boundary. For this reason, the sliding wall boundary condition has different definitions in different space dimensions. A single entry for the **Velocity of the tangentially moving wall** U_w should be specified in 2D.

CONSTRAINT SETTINGS

This section is displayed by clicking the **Show More Options** button (👁) and selecting **Advanced Physics Options.**

| 🔍 | Wall in the Single-Phase Flow interfaces |

Inlet

The **Inlet** node adds a set of boundary conditions that describe inlets in fluid-flow simulations.

MIXTURE BOUNDARY CONDITION

Select a **Mixture boundary condition** for the inlet — **Velocity** (the default) or **Pressure**.

VELOCITY

For **Velocity** click the **Normal inflow velocity** (the default) or **Velocity field** buttons.

- For **Normal inflow velocity** enter a value or expression for J_0 (SI unit: m/s).

- For **Velocity field** specify that the velocity at the boundary is equal to a given $\mathbf{j}_0$ (SI unit: m/s) and enter the components in the matrix:

$$\mathbf{j} = \mathbf{j}_0$$

PRESSURE

This condition specifies the normal stress which in most cases is approximately equal to the pressure. Enter the **Pressure** p_0 (SI unit: Pa) at the boundary. The default is 0 Pa. Enter a relative pressure value in p_0 (SI unit: Pa). Or if the reference pressure p_{ref} defined at the physics interface level is equal to 0 Pa, enter an absolute pressure in p_0.

- The **Suppress backflow** check box is selected by default. This option adjusts the inlet pressure, $\hat{p}_0 \geq p_0$, locally in order to reduce the amount of fluid exiting the domain through the boundary. If suppress backflow is deselected, the inlet boundary can become an outlet depending on the pressure field in the rest of the domain.

- **Flow direction** controls in which direction the fluid enters the domain.

  - For **Normal flow** (the default) it prescribes zero tangential velocity component.

  - For **User defined** define an **Inflow velocity direction**, $\mathbf{d_j}$ (dimensionless). The magnitude of $\mathbf{d_j}$ does not matter, only the direction. $\mathbf{d_j}$ must point into the domain.

DISPERSED PHASE BOUNDARY CONDITION

The default is **Dispersed phase concentration**. See Wall>Dispersed Phase Boundary Condition for the settings.

See Dispersed Phase Boundary Condition Equations for more information.

🔍	See Inlet in the Single-Phase Flow interfaces

Outlet

The **Outlet** node adds a selection of boundary conditions that describe outlets in fluid-flow simulations; that is, the conditions at boundaries where the fluid exits the domain.

MIXTURE BOUNDARY CONDITION

Select a **Mixture boundary condition** for the outlet — **Pressure** (the default) or **Velocity**.

PRESSURE CONDITIONS

The **Pressure** condition specifies the normal stress which in most cases is approximately equal to the pressure. The tangential stress component is set to 0 N/m^2.

- Enter the **Pressure** p_0 (SI unit: Pa) at the boundary. The default is 0 Pa. Enter a relative pressure value in p_0 (SI unit: Pa). Or if the reference pressure p_{ref} defined at the physics interface level is equal to 0 Pa, enter an absolute pressure in p_0.

- Select the **Normal flow** check box to change the no tangential stress condition to a no tangential velocity condition. This forces the flow to exit (or enter) the domain perpendicularly to the outlet boundary.

- The **Suppress backflow** check box is selected by default. This option adjusts the outlet pressure in order to reduce the amount of fluid entering the domain through the boundary.

VELOCITY

For **Velocity** click the **Normal outflow velocity** (the default) or **Velocity field** buttons.

- For **Normal outflow velocity** enter a value or expression for J_0 (SI unit: m/s).

- For **Velocity field** specify that the velocity at the boundary is equal to a given $\mathbf{j}_0$ (SI unit: m/s) and enter the components in the matrix:

$$\mathbf{j} = \mathbf{j}_0$$

DISPERSED PHASE BOUNDARY CONDITION

The default is **Dispersed phase outlet**. See Wall>Dispersed Phase Boundary Condition for the settings.

When the **Dispersed phase boundary condition** is set to **Dispersed phase outlet**, the **Exterior dispersed phase condition(s)** section contains an input field for the **Dispersed phase volume fraction** on the downstream side of the outlet. If **Solve for interfacial area** is selected at the physics interface level, additional input fields appear for the **Dispersed phase number density** or the **Diameter of particles/droplets** on the downstream side of the outlet.

See Dispersed Phase Boundary Condition Equations for more information.

⊚	See Outlet in the Single-Phase Flow interfaces

Symmetry

The **Symmetry** node adds boundary conditions that describe symmetry boundaries in fluid-flow simulations. The boundary condition for symmetry boundaries prescribes no penetration and vanishing tangential stress:

$$\mathbf{j} \cdot \mathbf{n} = 0, \qquad \mathbf{t}^T((\rho_c + \rho_d - \rho)\mathbf{u}_{\text{slip}}\mathbf{j}_{\text{slip}}^T + \tau_{\text{Gm}})\mathbf{n} = 0$$

BOUNDARY SELECTION

A boundary condition for 2D axial symmetry is not required.

For the symmetry axis at $r = 0$, the program automatically provides a condition that prescribes $u_r = 0$ and vanishing stresses in the z direction and adds an **Axial Symmetry** node that is valid on the axial symmetry boundaries only.

Periodic Flow Condition

The **Periodic Flow Condition** splits its selection into a source group and a destination group. Fluid that leaves the domain through one of the destination boundaries enters the domain through the corresponding source boundary. This corresponds to a situation where the geometry is a periodic part of a larger geometry. If the boundaries are not parallel to each other, the velocity vector is automatically transformed.

If the boundaries are curved, the orientation of the source must be specified manually (see Orientation of Source).

PRESSURE DIFFERENCE

A value or expression should be specified for the **Pressure difference**, $p_{src} - p_{dst}$. This pressure difference can, for example, drive the fully developed flow in a channel.

To set up a periodic boundary condition, both boundaries must be selected in the **Periodic Flow Condition** node. COMSOL Multiphysics automatically assigns one boundary as the source and the other as the destination. To manually set the destination selection, a **Destination Selection** subnode is available from the context menu (by right-clicking the parent node) or from the **Physics** toolbar, **Attributes** menu. All destination sides must be connected.

CONSTRAINT SETTINGS

This section is displayed by clicking the **Show More Options** button (👁) and selecting **Advanced Physics Options**.

ORIENTATION OF SOURCE

For information about the **Orientation of Source** section, see Orientation of Source and Destination in the *COMSOL Multiphysics Reference Manual*.

Interior Wall

The **Interior Wall** node adds a wall boundary condition on interior boundaries. It is similar to the Wall boundary condition available on exterior boundaries except that it applies on both sides of an interior boundary. It allows discontinuities of the dependent

variables across the boundary. The Interior Wall node specifies no flux for the dispersed phase.

Dispersed Phase Boundary Condition Equations

MIXTURE BOUNDARY CONDITION

Select a **Mixture boundary condition** — **No slip** (the default) or **Slip**.

No Slip
No slip is the default boundary condition for the mixture. A no slip wall is a wall where the mixture velocity relative to the wall velocity is zero. For an interior stationary wall, it sets the mixture velocity to zero at the wall:

$$\mathbf{j} = 0$$

Slip
Select **Slip** to set the velocity component normal to the wall to zero $\mathbf{j} \cdot \mathbf{n} = 0$.

Navier Slip
The **Navier slip** condition enforces no-penetration at the wall, $\mathbf{j} \cdot \mathbf{n} = 0$, and adds a friction force of the form

$$\mathbf{F}_{\text{fr}} = -\frac{\mu}{\beta}\mathbf{j}$$

where β is a slip length. For more information, see the **Navier Slip** option in the Wall feature.

WALL MOVEMENT

This section contains controls to describe the wall movement relative to the lab (or spatial) frame.

The **Translational velocity** setting controls the translational wall velocity, $\mathbf{u}_{\text{tr}}$. The list is per default set to **Automatic from frame**. The physics automatically detects if the spatial frame moves. This can for example happen if an ALE interface is present in the model component. If there is no movement $\mathbf{u}_{\text{tr}} = \mathbf{0}$. If the frame moves, $\mathbf{u}_{\text{tr}}$ becomes equal to the frame movement. $\mathbf{u}_{\text{tr}}$ is accounted for in the actual boundary condition prescribed in the **Boundary condition** section.

Select **Manual** from **Translational velocity** selection list in order to manually prescribe **Velocity of moving wall**, $\mathbf{u_{tr}}$. This can for example be used to model an oscillating wall where the magnitude of the oscillations are very small compared to the rest of the model. Specifying translational velocity manually does not automatically cause the associated wall to move. An additional Moving Mesh interface needs to be added to physically track the wall movement in the spatial reference frame.

CONSTRAINT SETTINGS

This section is displayed by clicking the **Show More Options** button (☞) and selecting **Advanced Physics Options.**

⊕	Wall

Mixture Continuity

The **Mixture Continuity** condition is suitable for pairs where the boundaries match; it prescribes that the flow field is continuous across the pair.

The parts of the boundary where a source boundary lacks a corresponding destination boundary and vice versa will get conditions from other boundary conditions under the physics interface acting as fallback boundary conditions on the nonoverlapping parts. By default, the Wall node is used as fallback unless another feature has been selected for the boundary.

⊕	About Identity and Contact Pairs

The Euler-Euler Model Interface

In this section:

The Euler–Euler Model, Laminar Flow Interface

The **Euler-Euler Model, Laminar Flow (ee)** interface (⬚), found under the **Multiphase Flow>Euler-Euler Model** branch (⬚) when adding a physics interface, can be used to simulate the flow of two continuous and fully interpenetrating incompressible phases (see Ref. 1 under the Theory for the Euler–Euler Model Interfaces). The physics interface can model flow at low and moderate Reynolds numbers. Typical applications are fluidized beds (solid particles in gas), sedimentation (solid particles in liquid), or transport of liquid droplets or bubbles in a liquid.

The physics interface solves two sets of Navier–Stokes equations, one for each phase, in order to calculate the velocity field for each phase. The phases interchange momentum as described by a drag model. The pressure is calculated from a mixture-averaged continuity equation and the volume fraction of the dispersed phase is tracked with a transport equation.

When this physics interface is added, the following default physics nodes are also added in the **Model Builder** — **Phase Properties**, **Wall**, and **Initial Values**. Then, from the **Physics** toolbar, add other nodes that implement, for example, boundary conditions and volume forces. You can also right-click **Euler-Euler Model, Laminar Flow** 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 `ee`.

DISPERSED PHASE

Select a **Dispersed phase** — **Solid particles** or **Liquid droplets/bubbles**.

When **Solid particles** is selected, the section is available in the Phase Properties node. Also see Dispersed Phase in the theory section.

PHYSICAL MODEL

Dispersed Phase
Select a **Dispersed phase** — **Solid particles** or **Liquid droplets/bubbles**.

When **Solid particles** is selected, the section is available in the Phase Properties node. Also see Dispersed Phase in the theory section.

Reference Values
Reference values are global quantities used to evaluate the density of the fluid and define the absolute pressure.

Reference pressure level There are generally two ways to include the pressure in fluid flow computations: either to use the absolute pressure $p_A = p + p_{ref}$, or the gauge pressure p. When p_{ref} is nonzero, the physics interface solves for the gauge pressure whereas material properties are evaluated using the absolute pressure. The reference pressure level is also used to define the density of incompressible fluids.

Reference temperature The reference temperature is used to define the reference density.

DEPENDENT VARIABLES

The dependent variables (field variables) are:

- **Velocity field, continuous phase uc**
- **Velocity field, dispersed phase ud**
- **Pressure** p
- **Volume fraction, dispersed phase** phid

The names can be changed but the names of fields and dependent variables must be unique within a component.

CONSISTENT STABILIZATION

To display this section, click the **Show More Options** button (👁) and select **Stabilization** in the **Show More Options** dialog box.

INCONSISTENT STABILIZATION

To display this section, click the **Show More Options** button (👁) and select **Stabilization** in the **Show More Options** dialog box.

Inconsistent stabilization can be activated independently for the momentum equation for the continuous phase, the momentum equation for the dispersed phase, and for the dispersed phase transport equation respectively by selecting the corresponding check box. Each inconsistent stabilization contribution has a tuning parameter.

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.

The **Residue volume fraction, continuous phase**, $\phi_{c,res}$, and **Residue volume fraction, dispersed phase**, $\phi_{d,res}$, set the smallest values used to avoid division by zero when evaluating terms that involve $1/\phi_c$ and $1/\phi_d$. Observe that this value does not prevent ϕ_c or ϕ_d from becoming smaller than $\phi_{c,res}$ and $\phi_{d,res}$, respectively.

Select the **Use pseudo time stepping for stationary equation form** check box to add pseudo time derivatives to the equation when the **Stationary equation** form is used. When selected, also choose a **CFL number expression** — **Automatic** (the default) or **Manual**. **Automatic** sets the local CFL number (from the Courant–Friedrichs–Lewy condition) to the built-in variable CFLCMP which in turn triggers a PID regulator for the CFL number. For **Manual** enter a **Local CFL number** CFL_{loc} (dimensionless).

DISCRETIZATION

The Euler-Euler Model, Laminar Flow interface supports three options for the basis functions: **P1+P1** (the default option), **P2+P1**, and **P3+P2**. They all represent Lagrangian basis functions of different orders:

- **P1+P1** – Linear basis functions for all degrees of freedom. Linear basis functions are computationally less expensive than the higher-order options and are also more robust. This option requires that **Streamline diffusion** is activated for both of the momentum equations.

- **P2+P1** – Quadratic basis functions for all degrees of freedom except the pressure which is described by linear basis functions. Higher order elements, as compared to linear elements, are a computationally effective way to obtain high accuracy but only

if the flow is well resolved. This requirement is most likely fulfilled for flows with very low velocities and/or small length scales.

- **P3+P2** – Cubic basis functions for all degrees of freedom except the pressure which is described by quadratic basis functions. This option is computationally very expensive and the least robust one but it is also the option with the highest formal accuracy.

To see all settings available in this section, click the **Show More Options** button (👁) and select **Advanced Physics Options**.

🔍	• Pseudo Time Stepping for Laminar Flow Models in this guide and Pseudo Time Stepping in the *COMSOL Multiphysics Reference Manual* • Isotropic Diffusion in the *COMSOL Multiphysics Reference Manual* • Domain, Boundary, Point, and Pair Nodes for the Euler–Euler Model Interfaces • Theory for the Euler–Euler Model Interfaces

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Domain, Boundary, Point, and Pair Nodes for the Euler–Euler Model Interfaces

 have the following domain, boundary, point, and pair nodes 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).

- Flow Continuity
- Gravity
- Initial Values
- Inlet
- Interior Wall

- Mass Transfer
- Outlet
- Phase Properties
- Volume Force
- Wall

The following nodes are described for the Laminar Flow interface:

- Pressure Point Constraint

- Symmetry

Phase Properties

The **Phase Properties** node has the material properties settings for the pure continuous and dispersed phases. It also has settings for the viscosity models for each of the two interpenetrating phases and the drag model. When the dispersed phase consists of solid particles, it also has settings for the solid pressure model.

MODEL INPUTS

Fluid properties, such as density and viscosity, can be defined through user inputs, variables, or by selecting a material. For the latter option, additional inputs, for example temperature or pressure, may be required to define these properties.

Temperature

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.

Absolute Pressure

This input appears when a material requires the absolute pressure as a model input. The absolute pressure is used to evaluate material properties, but it also relates to the value of the calculated pressure field. There are generally two ways to calculate the pressure when describing fluid flow: either to solve for the absolute pressure or for a pressure (often denoted gauge pressure) that relates to the absolute pressure through a reference pressure.

The default **Absolute pressure** p_A is $p + p_{ref}$, where p is the dependent pressure variable from the Navier–Stokes or RANS equations, and p_{ref} is from the user input defined at the physics interface level. When p_{ref} is nonzero, the physics interface solves for a gauge pressure. If the pressure field instead is an absolute pressure field, p_{ref} should be set to 0.

The **Absolute pressure** field can be edited by clicking **Make All Model Inputs Editable** (🖉) and entering the desired value in the input field.

ℚ	Model Inputs and Multiphysics Couplings in the *COMSOL Multiphysics Reference Manual*

MATERIALS

Select the materials to use for the material properties of the continuous phase and the dispersed phase respectively (when they are defined to take their values **From material**). By default, the default material used for the **Continuous phase** is the **Domain material**. This corresponds to the material currently applied to the domain in question. The **Dispersed phase** uses **None** per default. A valid material must be selected instead.

Other materials present can be selected from the **Continuous phase** or **Dispersed phase** list in order to use that material's properties for the liquid or gas, respectively.

CONTINUOUS PHASE PROPERTIES

Density, Continuous Phase
The default **Density, continuous phase** ρ_c (SI unit: kg/m^3) uses values **From material**. For **User defined** enter another value or expression.

Dynamic Viscosity, Pure Continuous Phase
The dynamic viscosity describes the relationship between the shear stresses and the shear rate in a fluid. Intuitively, water and air have a low viscosity, and substances often described as thick, such as oil, have a higher viscosity. The dynamic viscosity of the pure continuous phase refers to the viscosity the fluid would have in the absence of the dispersed phase.

The default **Dynamic viscosity, pure continuous phase** μ_c (SI unit: Pa·s) uses values **From material**. The value of the viscosity is then the value defined for the material selected in the **Materials** section for the continuous phase. For **User defined** define a different value or expression.

The default **Density, dispersed phase** ρ_d (SI unit: kg/m^3) uses values **From material**. For **User defined** enter another value or expression.

Enter a value or expression for the **Diameter of particles/droplets** d_d (SI unit: m). The default is 10^{-3} m (1 mm).

The **Dynamic viscosity, pure dispersed phase** μ_d (SI unit: Pa·s) field is available when **Liquid droplets/bubbles** is selected as the **Dispersed phase** in .

The default uses values **From material**. The value of the viscosity is then the value defined for the material selected in the **Materials** section for the dispersed phase. For **User defined** define a different value or expression.

VISCOSITY MODEL

Select a model for the **Mixture viscosity** — **Krieger type** (the default), **Volume average** (available for liquid droplets and bubbles) or **User defined**. Krieger type is appropriate for dispersed phases that do not form any pure phase regions. Volume average is more appropriate when the dispersed phase effectively can become the only phase in some regions.

- For **Krieger type**, select an option for **Maximum packing concentration.** The default is to use $\phi_{d,max} = 1.0$ for droplets and bubbles and $\phi_{d,max} = 0.62$ for particles. Select **User defined** to enter another value or expression for $\phi_{d,max}$.

- For **User defined** enter a value or expression for the **Mixture viscosity**. The default expression corresponds to the Krieger type viscosity with maximum packing equal to 0.62.

Select a **Dynamic viscosity model, continuous phase** — **Mixture viscosity** (default), **Pure phase value** or **User defined**. The **Mixture viscosity** option is appropriate when the maximum packing is controlled by the mixture viscosity. The **Pure phase value** option is more appropriate if the maximum packing is controlled in some other way, for example by solid pressure. Select **User defined** to enter an expression for the **Dynamic viscosity model, continuous phase**.

Select a **Dynamic viscosity model, dispersed phase** — **Mixture viscosity** (default), **Pure phase value** (available for bubbles and droplets), **Gidaspow** (available for solid particles) or **User defined**. The **Gidaspow** model prescribes $\mu_d^m = 0.5\phi_d$, which basically prescribes a small value for μ_d^m and should be combined with a solid pressure model.

DRAG MODEL

The models are described in . When the dispersed phase corresponds to **Solid particles**, the **Schiller–Naumann**, **Hadamard–Rybczynzki, Ishii–Zuber**, **Gidaspow**, and **Haider–Levenspiel** models are available. For **Liquid droplets/bubbles**, the **Schiller–Naumann**, **Hadamard–Rybczynzki, Ishii–Zuber**, and **Tomiyama et al.** models are available. Select the **User-defined drag coefficient** option to specify an expression for the drag coefficient C_D.

- The **Schiller–Naumann** is valid for dispersed, rigid spheres and can be used for particle Reynolds numbers less than approximately $2.5 \cdot 10^5$. The Schiller–Naumann model is a general purpose model for diluted flows.

- The **Hadamard–Rybczynzki** is appropriate for diluted flows at low Reynolds numbers.

- The **Ishii–Zuber** model can for solid particles be regarded as a generalization of the Schiller–Naumann model in that it can be used also for dense flows. For droplets and bubbles, the Ishii–Zuber model also takes deformation of the fluid particles into account. The deformation depends on the **Surface tension coefficient**, σ. Use a predefined expression, select **Library coefficient, liquid/gas interface** or **Library coefficient, liquid/liquid interface**. Then select an option from the list that displays below (for example, **Water/Air**, **Glycerol/Air** and so forth). For **User defined** enter a value or expression for the surface tension coefficient σ (SI unit: N/m).

- The **Gidaspow** model describes the drag force coefficient for dispersed phase flows for all concentrations of the dispersed solid, including high concentrations.

- The **Haider-Levenspiel** model describes nonspherical particles for low and moderate particle Reynolds numbers. Enter a value between 0 and 1 for the **Sphericity** S_p (dimensionless).

- The **Tomiyama et al.** model describes the drag for diluted droplets and bubbles for any particle Reynolds number. The correlation is available in three versions, **Pure fluid**, **Slightly contaminated fluid** and **Contaminated fluid**. The Tomiyama *et al.* model depends on the **Surface tension coefficient**, σ that is selected in the same way as for the Ishii–Zuber model.

SOLID PRESSURE MODEL

The solid pressure models the particle dispersion due to collisions and friction between the solid particles. Details of the implemented models are described in .

This section is available when **Solid particles** is selected as the **Dispersed phase** in . Select a **Solid pressure model** ∇p_s.

- The **No solid pressure** (the default) disables solid pressure and leaves the collision to be described by a mixture viscosity. This option is appropriate for solid suspension, typically solids suspended in liquids.

- The other options, **Gidaspow-Ettehadieh**, **Gidaspow**, **Ettehadieh**, and **User-defined modulus of elasticity** describes particle-particle interaction for dispersed solids, typically solid particles in gas flows. These options should be combined with the Gidaspow model or a small user-defined value for μ_d^m .

- For **User-defined modulus of elasticity** enter an expression for the **Modulus of elasticity**, G (SI unit: N/m^2).

MIXING LENGTH LIMIT

When the **Mixing length limit** $l_{\mathrm{mix,lim}}$ is set to **Automatic**, the mixing length limit is evaluated as the shortest side of the geometry bounding box. If the geometry is, for example, a complicated system of slim entities, this measure can be too high. In such cases, it is recommended that the mixing length limit is defined manually. Select **Manual** to enter a different value or expression.

Initial Values

The **Initial Values** node adds initial values for the velocity fields for the continuous and dispersed phases, the pressure, and the volume fraction of the dispersed phase that can serve as initial conditions for a transient simulation or as an initial guess for a nonlinear solver.

INITIAL VALUES

Enter initial values or expressions in the tables for each component of:

- **Velocity field, continuous phase uc**
- **Velocity field, dispersed phase ud**

Enter initial values or expressions for:

- **Pressure** p
- **Volume fraction, dispersed phase** phid

Mass Transfer

Use the **Mass Transfer** node to include mass transfer from the dispersed phase to the continuous phase.

MASS TRANSFER

Select a **Mass transfer model** — **User defined** (the default) or **Nonequilibrium model**. For **User defined** enter a value or expression for the **Mass transfer from dispersed to continuous phase** m_{dc} (SI unit: kg/(m^3·s)). The default is 0 kg/(m^3·s).

Nonequilibrium Model

For **Nonequilibrium model** enter values or expressions for each of the following:

- **Equilibrium volume fraction in dispersed phase** ϕ_{eq}. The default is 0.

- **Inverse time scales** f_c and f_d (SI unit: 1/s). The default is 0 s^{-1}.

The mass transfer is modeled as

$$m_{dc} = \rho_d[\max(f_c(\phi_d - \phi_{eq}), 0) - \max(f_d(\phi_{eq} - \phi_d), 0)]$$

Interphase Velocity

Select **Dispersed phase velocity field** (the default) or **User defined.** For **User defined** enter a value or expression for each component of the interphase velocity $\mathbf{u}_{int}$.

Gravity

The **Gravity** node adds the gravity force vector to the right-hand side of the momentum equations; $\rho_c\mathbf{g}$ for the continuous phase and $\rho_d\mathbf{g}$ for the dispersed phase.

Gravity nodes are mutually exclusive, that is, there can only be one active Gravity node per domain.

GRAVITY

Enter the components of the **Gravity vector**, $\mathbf{g}$ (SI unit: m/s^2). For 2D components the default Gravity vector is defined as (0,-g_const). Here g_const is a physical constant equal to 9.8066 m/s^2. For 3D and 2D axisymmetric components, the gravity acts in the negative z direction by default.

Volume Force

The **Volume Force** node specifies the volume forces on the right-hand side of the momentum equations; $\mathbf{F}_c$ for the continuous phase and $\mathbf{F}_d$ for the dispersed phase. It

may for example be used to add user defined interaction forces (in addition to the interphase drag force).

If several volume force nodes are added to the same domain, the sum of all contributions are added to the respective momentum equations.

Wall

The **Wall** node includes a set of boundary conditions to describe the flow conditions at a solid wall. The conditions for each phase are selected separately.

CONTINUOUS PHASE BOUNDARY CONDITION

Select a **Continuous Phase Condition** — **No slip** (the default), or **Slip**.

No Slip
A **No slip** condition models a wall where the velocity of the continuous phase relative to the wall velocity is zero. For a stationary wall, it sets the velocity of the continuous phase to zero:

$$\mathbf{u}_c = \mathbf{0}$$

For turbulent flows, wall functions are used to model the thin region near solid (no slip) walls with high gradients in the flow variables

Slip
The **Slip** option prescribes a no-penetration condition. For a stationary wall, $\mathbf{u}_c \cdot \mathbf{n} = 0$. It is implicitly assumed that there are no viscous effects at the slip wall and hence, no boundary layer develops.

Leakage
Select the **Leakage** check box to specify an **Inward continuous phase mass flux**, $\dot{m}_c$ (SI unit: kg/(m^2·s)). This option is intended for small values of $\dot{m}_c$. For large mass fluxes, select an Inlet feature instead.

DISPERSED PHASE BOUNDARY CONDITION

Select a **Dispersed velocity boundary condition** — **No slip** (the default), or **Slip**. The conditions prescribed for the velocity of the dispersed phase correspond to those described for the continuous phase above.

Dispersed Phase Boundary Condition

The **Dispersed Phase Boundary Condition** defines the condition at the wall for the volume fraction of the dispersed phase.

- **No dispersed phase flux** prescribes a zero flux condition at the wall.

- Select **Leakage** to prescribe an **Inward dispersed phase mass flux**, $\dot{m}_d$ (SI unit: kg/(m^2·s)). This option is intended for small values of $\dot{m}_d$. For large mass fluxes, select an Inlet feature instead.

WALL MOVEMENT

This section contains controls to describe the wall movement relative to the lab (or spatial) frame.

The **Translational velocity** setting controls the translational wall velocity, $\mathbf{u}_{tr}$. The list is per default set to **Automatic from frame**. The physics automatically detects if the spatial frame moves. This can for example happen if an ALE interface is present in the model component. If there is no movement $\mathbf{u}_{tr} = \mathbf{0}$. If the frame moves, $\mathbf{u}_{tr}$ becomes equal to the frame movement. $\mathbf{u}_{tr}$ is accounted for in the actual boundary condition prescribed in the **Boundary condition** section.

Select **Manual** from **Translational velocity** selection list in order to manually prescribe **Velocity of moving wall**, $\mathbf{u}_{tr}$. This can for example be used to model an oscillating wall where the magnitude of the oscillations are very small compared to the rest of the model. Specifying translational velocity manually does not automatically cause the associated wall to move. An additional Moving Mesh interface needs to be added to physically track the wall movement in the spatial reference frame.

The **Sliding wall** option is appropriate if the wall behaves like a conveyor belt; that is, the surface is sliding in its tangential direction. A velocity is prescribed at the wall and the boundary itself does not have to actually move relative to the reference frame.

- For 3D components, values or expressions for the **Velocity of sliding wall** $\mathbf{u}_w$ should be specified. If the velocity vector entered is not in the plane of the wall, COMSOL Multiphysics projects it onto the tangential direction. Its magnitude is adjusted to be the same as the magnitude of the vector entered.

- For 2D components, the tangential direction is unambiguously defined by the direction of the boundary. For this reason, the sliding wall boundary condition has different definitions in different space dimensions. A single entry for the **Velocity of the tangentially moving wall** U_w should be specified in 2D.

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

Inlet

The **Inlet** node prescribes the flow and turbulence conditions (when applicable) at a boundary where one or both phases enter the adjacent domain.

TWO-PHASE INLET TYPE

Selecting **Mixture** as the **Two-Phase Inlet Type**, inlet conditions are prescribed for both phases. Selecting **Continuous phase** or **Dispersed phase,** inlet conditions are prescribed for the corresponding phase, while wall conditions are applied to the remaining phase.

CONTINUOUS PHASE

The options available in this section are based on the **Two-phase inlet type** selected.

When **Mixture** or **Continuous phase** is selected as the **Two-phase inlet typ** the **Velocity field, continuous phase** $\mathbf{u}_{c0}$ is prescribed.

When **Dispersed phase** is selected as the **Two-phase inlet type**, the conditions applied to the continuous phase are **No slip** ($\mathbf{u}_c=\mathbf{0}$) or **Slip** ($\mathbf{u}_c\cdot\mathbf{n}=0$, and no viscous stresses in the tangential directions).

DISPERSED PHASE

The options available in this section are based on the **Two-phase inlet type** selected.

When **Mixture** or **Dispersed phase** is selected as the **Two-phase inlet type**, the **Velocity field, dispersed phase** $\mathbf{u}_{d0}$.

The **Dispersed phase boundary condition** can be **Volume fraction**, **Mass flux** or **No flux**.

- For **Volume fraction**, specify the **Dispersed phase volume fraction**, ϕ_{d0}, at the inlet. This option locks the value of ϕ_d, but the exact flux depends on the dispersed phase velocity, $\mathbf{u}_{d0}$.

- For **Mass flux**, prescribe describe the **Inward dispersed phase mass flux**, $\dot{m}_d$ (SI unit: kg/(m^2·s)). This option prescribes the flux for the dispersed phase, but the resulting volume fraction at the inlet depends on the dispersed phase velocity, $\mathbf{u}_{d0}$.

When **Continuous phase** is selected as the **Two-phase inlet type**, the conditions applied to the dispersed phase are **No slip** ($\mathbf{u}_d=\mathbf{0}$) or **Slip** ($\mathbf{u}_d\cdot\mathbf{n}=0$, and no viscous stresses in the tangential directions).

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

Outlet

This node is used to prescribe conditions at boundaries where the two-phase mixture exits the computational domain. The settings available in the node specifies conditions for the entire mixture, as opposed to the Inlet, Outlet and Wall nodes where the conditions for can be specified for each phase individually.

MIXTURE BOUNDARY CONDITION

Select **Mixture boundary conditions** — **Pressure, no viscous stress**, **Pressure**, **normal flow**, **Velocity**, **Degassing**, or **Filtration**.

Pressure Conditions
When **Pressure, no viscous stress** or **Pressure, normal flow** is selected as the **Mixture boundary condition**, specify the **Pressure** p_0 (SI unit: Pa) at the outlet. Note that the prescribed pressure should be consistent with the reference pressure level specified at the interface level as well as consistent with present volume forces (including gravity).

Velocity
Select **Velocity** to specify the **Velocity field, continuous phase** $\mathbf{u}_{c0}$ (SI unit: m/s) together with the **Velocity field, dispersed phase** $\mathbf{u}_d$ (SI unit: m/s) at the outlet.

Degassing and Filtration
Selecting **Degassing** allows the dispersed phase to exit the domain but prevents the continuous phase from exiting. This is achieved through a pressure (p_0), no viscous stress condition for the dispersed phase, in combination with a no penetration condition for the continuous phase.

Selecting **Filtration** on the other hand allows the continuous phase to exit the domain but prevents the dispersed phase from exiting. This is achieved through a pressure (p_0),

no viscous stress condition for the continuous phase, in combination with a no penetration condition for the dispersed phase.

📝　**Pressure, no viscous stress** is the least constraining option and allows the flow to exit the domain in nonnormal directions.

Pressure, normal flow restricts the flow to be completely normal to the outlet boundary. This option can influence the flow quite a bit upstream of the inlet.

CONSTRAINT SETTINGS

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

Interior Wall

The **Interior Wall** boundary condition can only be applied on interior boundaries.

It is similar to the Wall boundary condition available on exterior boundaries except that it applies on both sides of an interior boundary. It allows discontinuities of the dependent variables across the boundary. The **Interior Wall** boundary condition can be used to avoid meshing thin structures by applying no-slip conditions on interior curves and surfaces instead. Slip conditions and conditions for a moving wall can also be prescribed. It is compatible with laminar and turbulent flow. The conditions for each phase are selected separately.

CONTINUOUS PHASE BOUNDARY CONDITION

Select a **Continuous Phase Condition** — **No slip** (the default), or **Slip**.

No Slip
A **No slip** condition models a wall where the velocity of the continuous phase relative to the wall velocity is zero. For an interior stationary wall, it sets the velocity of the continuous phase to zero on both sides of the wall:

$$\mathbf{u}_c = \mathbf{0}$$

For turbulent flows, wall functions are used to model the thin region near solid walls with high gradients in the flow variables.

Slip

Slip prescribes a no-penetration condition. For a stationary interior wall, $\mathbf{u}_c \cdot \mathbf{n} = 0$ on both sides.

DISPERSED PHASE BOUNDARY CONDITION

Select a **Dispersed velocity boundary condition** — **No slip** (the default), or **Slip**. The conditions prescribed for the velocity of the dispersed phase correspond to those described for the continuous phase above.

Dispersed Phase Boundary Condition

The **Dispersed phase boundary condition** is set to **No dispersed phase flux**.

WALL MOVEMENT

This section contains controls to describe the wall movement relative to the lab (or spatial) frame.

The **Translational velocity** setting controls the translational wall velocity, $\mathbf{u}_{tr}$. The list is per default set to **Automatic from frame**. The physics automatically detects if the spatial frame moves. This can for example happen if an ALE interface is present in the model component. If there is no movement $\mathbf{u}_{tr} = \mathbf{0}$. If the frame moves, $\mathbf{u}_{tr}$ becomes equal to the frame movement. $\mathbf{u}_{tr}$ is accounted for in the actual boundary condition prescribed in the **Boundary condition** section.

Select **Manual** from **Translational velocity** selection list in order to manually prescribe **Velocity of moving wall**, $\mathbf{u}_{tr}$. This can for example be used to model an oscillating wall where the magnitude of the oscillations are very small compared to the rest of the model. Specifying translational velocity manually does not automatically cause the associated wall to move. An additional Moving Mesh interface needs to be added to physically track the wall movement in the spatial reference frame.

CONSTRAINT SETTINGS

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

Flow Continuity

The **Flow Continuity** condition is suitable for pairs where the boundaries match; it prescribes that the flow field is continuous across the pair.

The parts of the boundary where a source boundary lacks a corresponding destination boundary and vice versa will get conditions from other boundary conditions under the

physics interface acting as fallback boundary conditions on the nonoverlapping parts. By default, the Wall node is used as fallback unless another feature has been selected for the boundary.

About Identity and Contact Pairs

Theory for the Laminar Flow and Creeping Flow Interfaces

The theory for the Single-Phase Flow, Laminar Flow interface is described in this section:

- General Single-Phase Flow Theory
- Compressible Flow
- Weakly Compressible Flow
- The Mach Number Limit
- Incompressible Flow
- The Reynolds Number
- Gravity
- Theory for the Wall Boundary Condition
- Prescribing Inlet and Outlet Conditions
- Mass Flow
- Fully Developed Flow (Inlet)
- Fully Developed Flow (Outlet)
- No Viscous Stress
- Normal Stress Boundary Condition
- Porous Interface
- Mass Sources for Fluid Flow
- Numerical Stability — Stabilization Techniques for Fluid Flow
- Solvers for Laminar Flow
- Pseudo Time Stepping for Laminar Flow Models
- Nitsche Constraints
- Particle Tracing in Fluid Flow
- References for the Single-Phase Flow, Laminar Flow Interfaces

The theory about most boundary conditions is found in Ref. 2.

General Single-Phase Flow Theory

The Single-Phase Fluid Flow interfaces are based on the Navier–Stokes equations, which in their most general form read

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \tag{6-26}$$

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot [-p\mathbf{I} + \mathbf{K}] + \mathbf{F} \tag{6-27}$$

$$\rho C_p \left(\frac{\partial T}{\partial t} + (\mathbf{u} \cdot \nabla) T \right) = -(\nabla \cdot \mathbf{q}) + \mathbf{K}{:}\mathbf{S} - \frac{T}{\rho} \frac{\partial \rho}{\partial T}\bigg|_p \left(\frac{\partial p}{\partial t} + (\mathbf{u} \cdot \nabla) p \right) + Q \tag{6-28}$$

where

- ρ is the density (SI unit: kg/m^3)
- $\mathbf{u}$ is the velocity vector (SI unit: m/s)
- p is pressure (SI unit: Pa)
- $\mathbf{I}$ is the identity matrix (unitless)
- $\mathbf{K}$ is the viscous stress tensor (SI unit: Pa)
- $\mathbf{F}$ is the volume force vector (SI unit: N/m^3)
- C_p is the specific heat capacity at constant pressure (SI unit: J/(kg·K))
- T is the absolute temperature (SI unit: K)
- $\mathbf{q}$ is the heat flux vector (SI unit: W/m^2)
- Q contains the heat sources (SI unit: W/m^3)
- $\mathbf{S}$ is the strain-rate tensor:

$$\mathbf{S} = \frac{1}{2} (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)$$

The operation ":" denotes a contraction between tensors defined by

$$\mathbf{a}{:}\mathbf{b} = \sum_n \sum_m a_{nm} b_{nm} \tag{6-29}$$

This is sometimes referred to as the double dot product.

Equation 6-26 is the continuity equation and represents conservation of mass. Equation 6-27 is a vector equation which represents conservation of momentum.

Equation 6-28 describes the conservation of energy, formulated in terms of temperature. This is an intuitive formulation that facilitates boundary condition specifications.

To close the equation system, Equation 6-26 through Equation 6-28, constitutive relations are needed.

For a Newtonian fluid, which has a linear relationship between stress and strain, Stokes (Ref. 1) deduced the following expression:

$$\mathbf{K} = 2\mu\mathbf{S} - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I} \tag{6-30}$$

The dynamic viscosity, μ (SI unit: Pa·s), for a Newtonian fluid is allowed to depend on the thermodynamic state but not on the velocity field. All gases and many liquids can be considered Newtonian.

For an inelastic non-Newtonian fluid, the relationship between stress and strain rate is nonlinear, and an apparent viscosity is introduced instead of the dynamic viscosity. Examples of non-Newtonian fluids are honey, mud, blood, liquid metals, and most polymer solutions.

In theory, the same equations describe both laminar and turbulent flows. In practice, however, the mesh resolution required to simulate turbulence with the Laminar Flow interface makes such an approach impractical.

	There are several books where derivations of the Navier–Stokes equations and detailed explanations of concepts such as Newtonian fluids can be found. See, for example, the classical text by Batchelor (Ref. 3) and the more recent work by Panton (Ref. 4).

Many applications describe isothermal flows for which Equation 6-28 is decoupled from Equation 6-26 and Equation 6-27.

2D AXISYMMETRIC FORMULATIONS

A 2D axisymmetric formulation of Equation 6-26 and Equation 6-27 requires $\partial/\partial\phi$ to be zero. That is, there must be no gradients in the azimuthal direction. A common additional assumption is, however, that $u_\phi = 0$. In such cases, the ϕ-equation can be removed from Equation 6-27. The resulting system of equations is both easier to converge and computationally less expensive compared to retaining the ϕ-equation.

The default 2D axisymmetric formulation of Equation 6-26 and Equation 6-27 therefore assumes that

$$\partial / \partial \phi = 0$$
$$u_\phi = 0$$

Compressible Flow

The equations of motion for a single-phase fluid are the continuity equation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \tag{6-31}$$

and the momentum equation:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \nabla \cdot \left(\mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) \mathbf{I} \right) + \mathbf{F} \tag{6-32}$$

These equations are applicable for incompressible as well as for compressible flow with density and viscosity variations.

Weakly Compressible Flow

The same equations as for Compressible Flow are applied for weakly compressible flow. The only difference is that the density is evaluated at the reference pressure. The density may be a function of other quantities, in particular it may be temperature dependent.

The weakly compressible flow equations are valid for incompressible as well as compressible flow with density variations independent of the pressure.

Provided that the densities dependency pressure is specified through model inputs, the density is automatically evaluated at the reference pressure level.

The Mach Number Limit

An important dimensionless number in fluid dynamics is the Mach number, $\mathbf{Ma}$, defined by

$$\mathbf{Ma} = \frac{|\mathbf{u}|}{a}$$

where a is the speed of sound. A flow is formally incompressible when $\text{Ma} = 0$. This is theoretically achieved by letting the speed of sound tend to infinity. The Navier–Stokes equations then have the mathematical property that pressure disturbances are instantaneously propagated throughout the entire domain. This results in a parabolic equation system.

The momentum equation, Equation 6-32, is parabolic for unsteady flow and elliptic for steady flow, whereas the continuity equation, Equation 6-31, is hyperbolic for both steady and unsteady flow. The combined system of equations is thus hybrid parabolic-hyperbolic for unsteady flow and hybrid elliptic-hyperbolic for steady flow. An exception occurs when the viscous term in Equation 6-32 becomes vanishingly small, such as at an outflow boundary, in which case the momentum equation becomes locally hyperbolic. The number of boundary conditions to apply on the boundary then depends on the number of characteristics propagating into the computational domain. For the purely hyperbolic system, the number of characteristics propagating from the boundary into the domain changes as the Mach number passes through unity. Hence, the number of boundary conditions required to obtain a numerically well-posed system must also change. The compressible formulation of the laminar and turbulent interfaces uses the same boundary conditions as the incompressible formulation, which implies that the compressible interfaces are not suitable for flows with a Mach number larger than or equal to one. Yet, the practical Mach number limit is lower than one. The main reason is that the numerical scheme (stabilization and boundary conditions) of the Laminar Flow interface does not recognize the direction and speed of pressure waves. The fully compressible Navier–Stokes equations do, for example, start to display very sharp gradients already at moderate Mach numbers. But the stabilization for the single-phase flow interface does not necessarily capture these gradients. It is impossible to give an exact limit where the low Mach number regime ends and the moderate Mach number regime begins, but a rule of thumb is that the Mach number effects start to appear at $\text{Ma} = 0.3$. For this reason, the compressible formulation is referred to as *Compressible flow (Ma<0.3)* in COMSOL Multiphysics.

Incompressible Flow

When the temperature variations in the flow are small, a single-phase fluid can often be assumed incompressible; that is, ρ is constant or nearly constant. This is the case for all liquids under normal conditions and also for gases at low velocities. For constant ρ, Equation 6-31 reduces to

$$\rho \nabla \cdot \mathbf{u} = 0 \tag{6-33}$$

and Equation 6-32 becomes

$$\rho\frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla)\mathbf{u} = \nabla \cdot [-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T)] + \mathbf{F} \qquad (6\text{-}34)$$

Provided that the densities dependency on temperature and pressure is specified through model inputs, the density is evaluated at the reference pressure level and at the reference temperature. However, if the density is a function of other quantities such as a concentration field, or if the density is specified by a user defined expression, the user has to make sure that the density is defined as constant when the incompressible flow formulation is used.

The Reynolds Number

A fundamental characteristic in analyses of fluid flow is the Reynolds number:

$$\mathrm{Re} = \frac{\rho U L}{\mu}$$

where U denotes a velocity scale, and L denotes a representative length. The Reynolds number represents the ratio between inertial and viscous forces. At low Reynolds numbers, viscous forces dominate and tend to damp out all disturbances, which leads to laminar flow. At high Reynolds numbers, the damping in the system is very low, giving small disturbances the possibility to grow by nonlinear interactions. If the Reynolds number is high enough, the flow field eventually ends up in a chaotic state called turbulence.

Note that the Reynolds number can have different meanings depending on the length scale and velocity scale. To be able to compare two Reynolds numbers, they must be based on equivalent length and velocity scales.

The Fluid Flow interfaces automatically calculate the local cell Reynolds number $\mathrm{Re}^c = \rho|\mathbf{u}|h/(2\mu)$ using the element length h for L and the magnitude of the velocity vector u for the velocity scale U. This Reynolds number is not related to the character of the flow field, but to the stability of the numerical discretization. The risk for numerical oscillations in the solution increases as Re^c grows. The cell Reynolds number is a predefined quantity available for visualization and evaluation (typically it is available as: `spf.cellRe`).

Gravity

DEFINITION

The gravity force is defined from the acceleration of gravity vector, $\mathbf{g}$, and the density, ρ. Under usual conditions and in Cartesian coordinates with the z-axis in the vertical direction,

$$\mathbf{g} = \begin{pmatrix} 0 \\ 0 \\ -g_{\text{const}} \end{pmatrix}.$$

When gravity is considered, a volume force equal to $\rho\mathbf{g}$ is included in the momentum equation. For example, for laminar weakly compressible flow, it reads:

$$\rho\frac{\partial \mathbf{u}}{\partial t} + \rho\mathbf{u} \cdot \nabla\mathbf{u} = \nabla \cdot \left(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right) + \mathbf{F} + \rho\mathbf{g} \qquad (6\text{-}35)$$

Introducing a constant reference density ρ_{ref}, and assuming that $\mathbf{g}$ is homogeneous, this equation is equivalently written:

$$\rho\frac{\partial \mathbf{u}}{\partial t} + \rho\mathbf{u} \cdot \nabla\mathbf{u} =$$
$$\nabla \cdot \left(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I} + \rho_{\text{ref}}\mathbf{g} \cdot (\mathbf{r} - \mathbf{r}_{\text{ref}})\right) + \mathbf{F} + (\rho - \rho_{\text{ref}})\mathbf{g} \qquad (6\text{-}36)$$

where $\mathbf{r}$ is the position vector and $\mathbf{r}_{\text{ref}}$ is an arbitrary reference position vector.

From this equation, it is convenient to define the reduced pressure which accounts for the hydrostatic pressure, $\tilde{p} = p - \rho_{\text{ref}}\mathbf{g} \cdot (\mathbf{r} - \mathbf{r}_{\text{ref}})$

$$\rho\frac{\partial \mathbf{u}}{\partial t} + \rho\mathbf{u} \cdot \nabla\mathbf{u} = \nabla \cdot \left(-\tilde{p}\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right) +$$
$$\mathbf{F} + (\rho - \rho_{\text{ref}})\mathbf{g} \qquad (6\text{-}37)$$

In Equation 6-37, the gravity force is written $(\rho - \rho_{\text{ref}})\mathbf{g}$.

PRESSURE FORMULATION

When the relative pressure is used (default option) the interface dependent variable represents the relative pressure and the absolute pressure is defined as $p_A = p_{\text{ref}} + p$. When the pressure is used to define a boundary condition (for example, when p_0

defines the pressure condition at an outlet), it represents the relative pressure. Hence defining the outlet pressure as $p_{\text{hydro,approx}} = -\rho_{\text{ref}}\mathbf{g} \cdot (\mathbf{r} - \mathbf{r}_{\text{ref}})$ compensates for the gravity force for an ambient reference pressure of 0 Pa when the density is constant, there is no external force, and provided p_{ref}, $\mathbf{g}$, and $\mathbf{r}_0$ are defined consistently.

When the reduced pressure is used, the interface dependent variable (named p by default) represents the reduced pressure. The absolute pressure is then defined as $p_A = p_{\text{ref}} - \rho_{\text{ref}}\mathbf{g} \cdot (\mathbf{r} - \mathbf{r}_{\text{ref}}) + p$. In this case when the pressure is used to define a boundary condition (for example, to define a pressure condition at an outlet), its value corresponds to the reduced pressure. Hence, the prescribed pressure compensates for an approximate hydrostatic pressure, $p_{\text{hydro,approx}} = -\rho_{\text{ref}}\mathbf{g} \cdot (\mathbf{r} - \mathbf{r}_{\text{ref}})$, which is exact only when the density is constant and there is no external force.

PRESSURE BOUNDARY CONDITION

For an immobile fluid the momentum equation simplifies to $\nabla \cdot (p\mathbf{I}) = \mathbf{F} + \rho\mathbf{g}$ or

$$\nabla \cdot (-\tilde{p}\mathbf{I}) = \mathbf{F} + (\rho - \rho_{\text{ref}})\mathbf{g}$$ depending on the pressure formulation.

For incompressible flow, assuming there are no external forces, this leads respectively to $p = -\rho_{\text{ref}}\mathbf{g} \cdot (\mathbf{r} - \mathbf{r}_{\text{ref}}) + p_0$ or $\tilde{p} = p_0$.

Theory for the Wall Boundary Condition

See Wall for the node settings.

SLIP

The Slip condition assumes that there are no viscous effects at the slip wall and hence, no boundary layer develops. From a modeling point of view, this is a reasonable approximation if the important effect of the wall is to prevent fluid from leaving the domain. Mathematically, the constraint can be formulated as:

$$\mathbf{u} \cdot \mathbf{n} = 0, \qquad (-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T))\mathbf{n} = \mathbf{0}$$

The no-penetration term takes precedence over the Neumann part of the condition and the above expression is therefore equivalent to

$$\mathbf{u} \cdot \mathbf{n} = 0, \qquad \mathbf{K}_n - (\mathbf{K}_n \cdot \mathbf{n})\mathbf{n} = \mathbf{0}$$
$$\mathbf{K}_n = \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T)\mathbf{n}$$

expressing that there is no flow across the boundary and no viscous stress in the tangential direction.

For a moving wall with translational velocity $\mathbf{u}_{tr}$, $\mathbf{u}$ in the above equations is replaced by the relative velocity $\mathbf{u}_{rel} = \mathbf{u} - \mathbf{u}_{tr}$.

POROUS SLIP

The **Porous slip** option, which can be chosen in the **Porous treatment of no slip condition** list when **Enable porous media domains** is activated, results in a special treatment of **Wall** boundaries and **Interior Wall** boundaries adjacent to porous domains (**Porous Medium** feature). Namely, similar to the **Navier slip** boundary condition, no penetration and tangential stress conditions are applied at the wall:

$$\mathbf{u} \cdot \mathbf{n} = 0, \quad \mathbf{K}_n - (\mathbf{K}_n \cdot \mathbf{n})\mathbf{n} = -\frac{\mu}{\varepsilon_p}\frac{\mathbf{u}_{slip}}{y_{ps}},$$

$$\mathbf{u}_{slip} = \mathbf{u} - (\mathbf{u} \cdot \mathbf{n})\mathbf{n}, \quad \mathbf{K}_n = \frac{\mu}{\varepsilon_p}(\nabla\mathbf{u} + (\nabla\mathbf{u})^T)\mathbf{n}$$

Here, $\mathbf{K}_n$ is the viscous wall traction, $\mathbf{n}$ is the wall normal, $\mathbf{u}_{slip}$ is the tangential velocity at the wall while real no slip is assumed to be applied at a distance d_w (half-height of the first cell adjacent to the wall) outside the wall, and is the porous slip length. An analytical derivation of the velocity profile in the boundary layer where the pressure gradient is balanced by the sum of the Darcy term, the Forchheimer drag, and the viscous term (neglecting convective terms) leads to the following expression for y_{ps}:

$$y_{ps} = \tilde{l}\left(\frac{1 + X_p e^{-\xi_p}}{1 - X_p e^{-\xi_p}}\right)\left[\left(\frac{1 + X_p e^{-\xi_p}}{1 + X_p}\right)^2 e^{\xi_p} - 1\right], \quad \xi_p = \frac{d_w}{\tilde{l}}, \quad \tilde{l} = \frac{l_{pore}}{\sqrt{1 + 2c_\beta}},$$

$$X_p = \frac{\sqrt{1 + 2c_\beta} - \sqrt{1 + \frac{4}{3}c_\beta}}{\sqrt{1 + 2c_\beta} + \sqrt{1 + \frac{4}{3}c_\beta}}, \quad c_\beta = \frac{\sqrt{1 + 4c_D} - 1}{2}, c_D = \frac{\beta_{ND}}{\mu}\frac{\kappa^2}{\mu}|\nabla p - \rho\mathbf{g}|$$

where $l_{pore} = \sqrt{\kappa/\varepsilon_p}$ is the porous length scale, $\beta_{ND} = \rho c_F/\sqrt{\kappa}$ is the non-Darcian coefficient (c_F is the Forchheimer coefficient), $\mathbf{g}$ is the gravity vector, and $\xi_p, l, X_p, c_\beta,$ c_D, are intermediate variables. This formula is used when the **Pressure-gradient formulation** is chosen and it uses the pressure gradient at the wall. By default, the **Velocity formulation** is activated and the corresponding formula is:

$$y_{ps} = \tilde{l}(e^{\xi_p} - 1), \quad \xi_p = \frac{d_w}{\tilde{l}}, \quad \tilde{l} = \frac{l_{pore}}{\sqrt{1 + 2c_\beta}},$$

$$c_\beta = \left[\left(\frac{\beta_{ND}\kappa|\mathbf{u}_{slip}|}{\mu}\frac{l_{pore}}{d_w}\right)^2/2\right]^{1/3}$$

Although this formulation is an approximation, since it uses the slip velocity at the wall to reconstruct the pressure gradient, it is rather accurate. Moreover, the influence of the convective terms is partially accounted for in this formulation.

SLIDING WALL

The sliding wall option is appropriate if the wall behaves like a conveyor belt; that is, the surface is sliding in its tangential direction. The wall does not have to actually move in the coordinate system.

- In 2D, the tangential direction is unambiguously defined by the direction of the boundary, but the situation becomes more complicated in 3D. For this reason, this boundary condition has slightly different definitions in the different space dimensions.

- For 2D and 2D axisymmetric components, the velocity is given as a scalar U_w and the condition prescribes

$$\mathbf{u} \cdot \mathbf{n} = 0, \qquad \mathbf{u} \cdot \mathbf{t} = U_w$$

where $\mathbf{t} = (n_y, -n_x)$ for 2D and $\mathbf{t} = (n_z, -n_r)$ for axial symmetry.

- For 3D components, the velocity is set equal to a given vector $\mathbf{u}_w$ projected onto the boundary plane:

$$\mathbf{u} = \frac{\mathbf{u}_w - (\mathbf{n} \cdot \mathbf{u}_w)\mathbf{n}}{\|\mathbf{u}_w - (\mathbf{n} \cdot \mathbf{u}_w)\mathbf{n}\|} \|\mathbf{u}_w\|$$

The normalization makes $\mathbf{u}$ have the same magnitude as $\mathbf{u}_w$ even if $\mathbf{u}_w$ is not exactly parallel to the wall.

Navier Slip

This boundary condition enforces no-penetration at the wall, $\mathbf{u} \cdot \mathbf{n}_{wall} = 0$, and adds a tangential stress

$$\mathbf{K}_{nt} = -\frac{\mu}{\beta}\mathbf{u}_{slip}$$

where $\mathbf{K}_{nt} = \mathbf{K}_n - (\mathbf{K}_n \cdot \mathbf{n}_{wall})\mathbf{n}_{wall}$, $\mathbf{K}_n = \mathbf{K}\mathbf{n}_{wall}$, and $\mathbf{K}$ is the viscous stress tensor. β is a slip length, and $\mathbf{u}_{slip} = \mathbf{u} - (\mathbf{u} \cdot \mathbf{n}_{wall})\mathbf{n}_{wall}$ is the velocity tangential to the wall. The boundary condition does not set the tangential velocity component to zero; however, the extrapolated tangential velocity component is 0 at a distance β outside the wall.

The **Slip Length** setting is per default set to **Factor of minimum element length**. The slip length β is then defined as $\beta = f_h h_{min}$, where h_{min} is the smallest element side

(corresponds to the element size in the wall normal direction for boundary layer elements) and f_h is a user input.

In cases where the wall movement is nonzero, **Account for the translational wall velocity in the friction force** may be selected to use $\mathbf{u} - \mathbf{u}_{bnd} - ((\mathbf{u} - \mathbf{u}_{bnd}) \cdot \mathbf{n}_{wall})\mathbf{n}_{wall}$ instead of $\mathbf{u}_{slip}$ in the friction force. Then, the extrapolated tangential velocity component is $\mathbf{u}_{bnd}$ at a distance β outside of the wall. Note that the **Velocity of sliding wall $\mathbf{u}_w$** is always accounted for in the friction force.

The Navier Slip option is not available when selecting a turbulence model.

CONSTRAINT SETTINGS

The wall feature uses three different techniques to constraint the velocity field:

- **Pointwise constraints** is the standard technique to enforce strong constraints in the finite element method. The desired value of the velocity is prescribed at each node point in the mesh. Since the constraint is enforced locally at each node, only local values are affected by the constraint and the constraints are independent of each other. The solvers can therefore eliminate both the constrained degrees of freedom and the constraint force terms, effectively reducing the number of degrees of freedom being solved for.

  The main advantage of pointwise constraints is that they enforce the constraint exactly pointwise. This means that they do not introduce any leakage of the velocity across the wall, unless specified. The main disadvantage of pointwise constraints is that they introduce locking effects when trying to impose a no-penetration condition for the velocity, $\mathbf{u} \cdot \mathbf{n} = 0$, on curved walls or walls with sharp corners.

- **Weak constraints** is an alternative method to prescribe the velocity. It consists on enforcing the boundary condition for the velocity via *Lagrange multipliers*. Their main advantage is that the Lagrange multiplier can provide an accurate representation of the reaction flux at the wall. Their main disadvantage is that they introduce extra unknowns, and are usually difficult to combine with other constraint methods on adjacent boundaries. Moreover, they may require extra constraints for the Lagrange multipliers. For more information, see Weak Constraints in the *COMSOL Multiphysics Reference Manual*.

- **Nitsche constraints** use a numerical flux to prescribe the velocity at the wall. They impose the constraint in an integral sense rather than pointwise, and do not suffer from the locking effects introduced by pointwise constraints when trying to prescribe a no penetration condition for the velocity. They are also better behaved when prescribing nonlinear constraints. Their main disadvantage is that the

constraint is only imposed approximately, and may produce small leaks. For more information, see Nitsche Constraints.

The following combination of Constraint techniques can be selected in the **Constraint Setting** sections of Wall boundary conditions:

- **Automatic** (default) use different constraint methods depending on whether only the normal component of the velocity is prescribed, such as in the no penetration condition, $\mathbf{u} \cdot \mathbf{n} = 0$, imposed, for example, in Slip walls or No Slip walls using Wall Functions or Automatic Wall Treatment, or both tangential and normal components are prescribed, as is the case of No Slip walls in laminar flow.

  Nitsche constraints are used to impose the no penetration condition for Slip walls. When a No Slip condition is prescribed, pointwise constraints are used except for moving walls where Nitsche constraints are used.

- **Pointwise constraints**.
- **Nitsche constraints**.
- **Weak constraints**. They are not available on Interior Walls.
- **Mixed constraints**. This option is only available when both the tangential and normal components of the velocity need to be prescribed. The velocity on the wall normal direction is imposed via pointwise constraints. The constraint for the tangential directions is relaxed, and Nitsche constraints are used instead. This provides improved accuracy and performance when working with coarse boundary layer meshes. For more information, see Ref. 18.

Prescribing Inlet and Outlet Conditions

The Navier–Stokes equations can show large variations in mathematical behavior, ranging from almost completely elliptic to almost completely hyperbolic. This has implications when it comes to prescribing admissible boundary conditions. There is also a discrepancy between mathematically valid boundary conditions and practically useful boundary conditions. See Inlet and Outlet for the node settings.

INLET CONDITIONS

An inlet requires specification of the velocity components. The most robust way to do this is to prescribe a velocity field using a Velocity condition.

A common alternative to prescribing the complete velocity field is to prescribe a pressure and all but one velocity component. The pressure cannot be specified

pointwise because this is mathematically over-constraining. Instead the pressure can be specified via a stress condition:

$$-p + 2\mu\frac{\partial u_n}{\partial n} = F_n \tag{6-38}$$

where $\partial u_n/\partial n$ is the normal derivative of the normal velocity component. Equation 6-38 is prescribed by the Pressure condition in the Inlet and Outlet features and the Normal stress condition in the Open Boundary and Boundary Stress features. Equation 6-38 is mathematically more stringent compared to specifying the pressure pointwise and at the same time cannot guarantee that p obtains the desired value. In practice, p is close to F_n, except for low Reynolds number flows where viscous effects are the only effects that balance the pressure. In addition to Equation 6-38, all but one velocity component must be specified. For low Reynolds numbers, this can be specified by a vanishing tangential stress condition:

$$\mu\frac{\partial u_t}{\partial n} = 0$$

which is what the Normal stress condition does. Vanishing tangential stress becomes a less well-posed inlet condition as the Reynolds number increases. The Pressure condition in the Inlet feature therefore requires a flow direction to be prescribed, which provides a well-posed condition independent of Reynolds number.

OUTLET CONDITIONS

The most common approach is to prescribe a pressure via a normal stress condition on the outlet. This is often accompanied by a vanishing tangential stress condition:

$$\mu\frac{\partial u_t}{\partial n} = 0$$

where $\partial u_t/\partial n$ is the normal derivative of the tangential velocity field. It is also possible to prescribe u_t to be zero. The latter option should be used with care since it can have a significant effect on the upstream solution.

The elliptic character of the Navier–Stokes equations mathematically permits specifying a complete velocity field at an outlet. This can, however, be difficult to apply in practice. The reason being that it is hard to prescribe the outlet velocity so that it is consistent with the interior solution at each point. The adjustment to the specified velocity then occurs across an outlet boundary layer. The thickness of this boundary

layer depends on the Reynolds number; the higher the Reynolds number, the thinner the boundary layer.

ALTERNATIVE FORMULATIONS

COMSOL provides several specialized boundary conditions that either provide detailed control over the flow at the boundary or that simulate specific devices. In practice they often prescribe a velocity or a pressure but calculate the prescribed values using, for example, ODEs.

| ⓔ | Normal Stress Boundary Condition |

Mass Flow

The **Mass flow** boundary condition constrains the mass flowing into the domain across an inlet boundary. The mass flow can be specified in a number of ways.

POINTWISE MASS FLUX

The pointwise mass flux sets the velocity at the boundary to:

$$\mathbf{u} = -\frac{m_f}{\rho}\mathbf{n}$$

where m_f is the normal mass flux and ρ is the density.

MASS FLOW RATE

The mass flow rate boundary condition sets the total mass flow through the boundary according to:

$$-\int_{\partial\Omega} d_{bc}\rho(\mathbf{u}\cdot\mathbf{n})\mathrm{d}S = m$$

where d_{bc} (only present in the 2D Cartesian axis system) is the boundary thickness normal to the fluid-flow domain and m is the total mass flow rate.

In addition to the constraint on the total flow across the boundary, the tangential velocity components are set to zero on the boundary

$$\mathbf{u}\times\mathbf{n} = 0 \tag{6-39}$$

STANDARD FLOW RATE

The standard flow rate boundary condition specifies the mass flow as a standard volumetric flow rate. The mass flow through the boundary is set by the equation:

$$-\int_{\partial\Omega} d_{bc}\frac{\rho}{\rho_{st}}(\mathbf{u}\cdot\mathbf{n})dS = Q_{sv}$$

where d_{bc} (only present in the 2D component Cartesian axis system) is the boundary thickness normal to the fluid-flow domain, ρ_{st} is the standard density, and Q_{sv} is the standard flow rate. The standard density is defined by one of the following equations:

$$\rho_{st} = \frac{M_n}{V_n}$$

$$\rho_{st} = \frac{p_{st}M_n}{RT_{st}}$$

where M_n is the mean molar mass of the fluid, V_n is the standard molar volume, p_{st} is the standard pressure, R is the universal molar gas constant, and T_{st} is the standard temperature.

Equation 6-39 or Equation 6-40 is also enforced for compressible and incompressible flow, respectively, ensuring that the normal component of the viscous stress and the tangential component of the velocity are zero at the boundary.

Fully Developed Flow (Inlet)

The **Fully developed flow** boundary condition can be understood from the following figure:
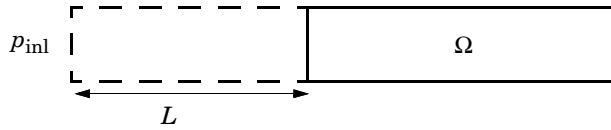
The flow to the domain Ω is assumed to enter through a straight channel of length L. The channel is a virtual extrusion of the inlet cross section and a pressure constant pressure P_{inl} is applied on the inlet of the virtual channel.

The Fully Developed Flow boundary condition prescribes that the tangential flow component on the boundary is zero:

$$\mathbf{u} - (\mathbf{u} \cdot \mathbf{n})\mathbf{n} = \mathbf{0}$$

The momentum equation for a fully developed flow in the virtual extrusion of the inlet cross section can then be projected onto the inlet boundary with the following weak equation as the result:

$$\int_{\partial\Omega} \left(\left(L\left(-\mu(\nabla_{\mathbf{t}}\mathbf{u} + (\nabla_{\mathbf{t}}\mathbf{u})^T) + \frac{(p + P_{\text{inl}})}{2}\mathbf{I}\right):(\nabla_{\mathbf{t}}\hat{\mathbf{u}})\right) - P_{\text{inl}}(\mathbf{n} \cdot \hat{\mathbf{u}}) \right)$$

The exact value of L is somewhat arbitrary as long as it is not too high or too low. L is therefore set to ten times the inlet edge length in 2D and to ten times the square root of the inlet area in 2D axisymmetry and in 3D.

The fact that the velocity profile is not prescribed, but rather the solution of a projected weak contribution, means that the actual velocity profile that is obtained on the inlet can deviate from the analytical fully developed flow profile (in cases such an analytical solution exists) if required by the solution inside the computational domain, Ω. This is most notably if the flow is strongly curved just downstream of the inlet. This can, for example, be the case if an object is positioned just downstream of the inlet or if the adjacent boundaries are not orthogonal to the inlet. The analytical solution can in these cases be recovered by including a little bit of the inlet channel in the computational domain.

The inlet pressure, P_{inl}, must be solved for and the its equation is a discrete algebraic equation (DAE) for P_{inl}. When, for example, the average velocity is specified, the DAE reads

$$(\langle \mathbf{u} \cdot \mathbf{n} \rangle + U_{\text{av}})\hat{P}_{\text{inl}}$$

where <·> denotes the average over the inlet. Since the equation for P_{inl} is a DAE (the equation for P_{inl} does not contain P_{inl}), it must be solved coupled to Navier–Stokes and it must be treated by a Vanka presmoother and postsmoother if iterative solvers are used.

The boundary conditions for the virtual inlet channel are inherited from the boundaries adjacent to the inlet channel. Virtual boundaries adjacent to walls (except slip walls) are treated as no-slip walls. Virtual boundaries adjacent to any other type of boundary are treated as slip-walls (or equivalently as symmetry boundaries). So in the figure above, if the lower boundary of Ω is a no-slip wall and the top boundary is a symmetry boundary, the lower boundary of the virtually extruded channel becomes a no-slip wall and the upper boundary becomes a symmetry boundary.

Algebraic turbulence models need to additional equations or constraints. For all other turbulence models, their weak equations in the virtual inlet channel are projected onto the inlet of the computational domain. The projections are regularized to prevent the production to fall to zero, so the solutions of the projects can show slight deviation from the correct solutions close to no-slip walls.

Fully Developed Flow (Outlet)

The **Fully developed flow** boundary condition can be understood from the following figure:
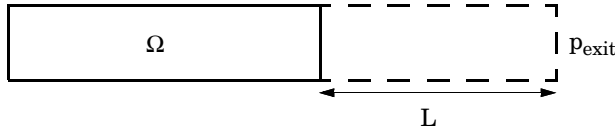
The flow to the domain Ω is assumed to enter through a straight channel of length L. The channel is a virtual extrusion of the inlet cross section and a pressure constant pressure P_{exit} is applied on the inlet of the virtual channel.

The Fully Developed Flow boundary condition prescribes that the tangential flow component on the boundary is zero:

$$\mathbf{u} - (\mathbf{u} \cdot \mathbf{n})\mathbf{n} = \mathbf{0}$$

The momentum equation for a fully developed flow in the virtual extrusion of the inlet cross section can then be projected onto the inlet boundary with the following weak equation as the result:

$$\int_{\partial\Omega} \left(\left(L \left(-\mu(\nabla_{\mathbf{t}}\mathbf{u} + (\nabla_{\mathbf{t}}\mathbf{u})^T) + \frac{(p + P_{exit})}{2}\mathbf{I} \right) : (\nabla_{\mathbf{t}}\hat{\mathbf{u}}) \right) - P_{exit}(\mathbf{n} \cdot \hat{\mathbf{u}}) \right)$$

The exact value of L is somewhat arbitrary as long as it is not too high or too low. L is therefore set to ten times the inlet edge length in 2D and to ten times the square root of the inlet area in 2D axisymmetry and in 3D.

The fact that the velocity profile is not prescribed, but rather the solution of a projected weak contribution, means that the actual velocity profile that is obtained on the outlet can deviate from the analytical fully developed flow profile (in cases such an analytical solution exists) if required by the solution inside the computational domain, Ω. The inlet pressure, P_{exit}, must be solved for and the its equation is a discrete algebraic

equation (DAE) for P_{exit}. When, for example, the average velocity is specified, the DAE reads

$$(\langle \mathbf{u} \cdot \mathbf{n} \rangle + U_{av})\hat{P}_{exit}$$

where <·> denotes the average over the inlet. Since the equation for P_{ext} is a DAE, it must be solved coupled to Navier–Stokes and it must be treated by a Vanka presmoother and postsmoother if iterative solvers are used.

The boundary conditions for the virtual outlet channel are inherited from the boundaries adjacent to the outlet channel. Virtual boundaries adjacent to walls (except slip walls) are treated as no-slip walls. Virtual boundaries adjacent to any other type of boundary are treated as slip-walls (or equivalently as symmetry boundaries).

No Viscous Stress

For this module, and in addition to the Pressure, No Viscous Stress boundary condition, the viscous stress condition sets the viscous stress to zero:

$$\left(\mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right)\mathbf{n} = \mathbf{0}$$

$$(\mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T))\mathbf{n} = \mathbf{0}$$

using the compressible/weakly compressible and the incompressible formulation, respectively.

The condition is not a sufficient outlet condition since it lacks information about the outlet pressure. It must hence be combined with pressure point constraints on one or several points or lines surrounding the outlet.

This boundary condition is numerically the least stable outlet condition, but can still be beneficial if the outlet pressure is nonconstant due to, for example, a nonlinear volume force.

Normal Stress Boundary Condition

The total stress on the boundary is set equal to a stress vector of magnitude f_0, oriented in the negative normal direction:

$$\left(-p\mathbf{I} + \left(\mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right)\right)\mathbf{n} = -f_0\mathbf{n}$$

$$(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T))\mathbf{n} = -f_0\mathbf{n}$$

using the compressible/weakly compressible and the incompressible formulation, respectively.

This implies that the total stress in the tangential direction is zero. This boundary condition implicitly sets a constraint on the pressure which for 2D flows is

$$p = 2\mu\frac{\partial u_n}{\partial n} + f_0 \tag{6-40}$$

If $\partial u_n/\partial n$ is small, Equation 6-40 states that $p \approx f_0$.

The Normal Stress condition is the mathematically correct version of the Pressure Conditions condition (Ref. 4), but it is numerically less stable.

Pressure Boundary Condition

For single-phase flow, a mathematically correct natural boundary condition for outlets is

$$\left(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla\cdot\mathbf{u})\mathbf{I}\right)\mathbf{n} = -p_0\mathbf{n} \tag{6-41}$$

$$(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T))\mathbf{n} = -p_0\mathbf{n} \tag{6-42}$$

using the compressible/weakly compressible and the incompressible formulation, respectively.

This is a normal stress condition together with a no-tangential-stress condition. When $\mu > 0$, Equation 6-41 or Equation 6-42 can be supplemented with a tangential velocity condition

$$\mathbf{u}\cdot\mathbf{t} = 0 \tag{6-43}$$

If so, the no-tangential-stress condition is overridden. An issue with Equation 6-41 or Equation 6-42 is that it does not strongly enforce unidirectional flow on the boundary. If the prescribed pressure on an outlet is too high, parts of the outlet can actually have inflow. This is not as much of an issue for the Navier–Stokes equations as it is an issue for scalar transport equations solved along with the Navier–Stokes equations. Hence, when applying the **Pressure** boundary condition at an outlet or inlet you can further constrain the flow. With the **Suppress backflow** option

$$\left(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla\cdot\mathbf{u})\mathbf{I}\right)\mathbf{n} = -\hat{p}_0\mathbf{n}$$

$$(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T))\mathbf{n} = -\hat{p}_0\mathbf{n}$$

$$\hat{p}_0 \le p_0$$

(6-44)

the normal stress is adjusted to keep

$$\mathbf{u}\cdot\mathbf{n} \ge 0 \tag{6-45}$$

Equation 6-44 effectively means that the prescribed pressure is p_0 if $\mathbf{u}\cdot\mathbf{n} \ge 0$, but smaller at locations where $\mathbf{u}\cdot\mathbf{n} < 0$. This means that Equation 6-44 does not completely prevent backflow, but the backflow is substantially reduced. Backflow is suppressed also when external forces are acting on the fluid, provided the magnitude of these forces are of the same order as the dynamic pressure at the outlet.

A pressure condition can also be applied at an inlet. In this case, either the normal stress is prescribed

$$\mathbf{n}^T\left(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla\cdot\mathbf{u})\mathbf{I}\right)\mathbf{n} = -\hat{p}_0$$

$$\mathbf{n}^T(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T))\mathbf{n} = -\hat{p}_0$$

$$\hat{p}_0 \ge p_0$$

(6-46)

together with the tangential condition in Equation 6-43, or, a general flow direction is prescribed.

$$\mathbf{r}_\mathbf{u}^T\left(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla\cdot\mathbf{u})\mathbf{I}\right)\mathbf{n} = -\hat{p}_0(\mathbf{r}_\mathbf{u}\cdot\mathbf{n})$$

$$\mathbf{r}_\mathbf{u}^T(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T))\mathbf{n} = -\hat{p}_0(\mathbf{r}_\mathbf{u}\cdot\mathbf{n})$$

$$\hat{p}_0 \ge p_0$$

$$\mathbf{u} - (\mathbf{u}\cdot\mathbf{r}_\mathbf{u})\mathbf{r}_\mathbf{u} = \mathbf{0}, \ \mathbf{r}_\mathbf{u} = \frac{\mathbf{d}_\mathbf{u}}{\|\mathbf{d}_\mathbf{u}\|}$$

(6-47)

The ">" option is used with suppress backflow to have $\mathbf{u}\cdot\mathbf{n} \le 0$ or $\mathbf{u}\cdot\mathbf{r}_\mathbf{u} \ge 0$.

For incompressible single-phase flow, it is also allowed to specify the total pressure, p_{tot}, instead of the static pressure, p_{stat}, on inlet and outlet boundaries. It is more

useful, for example, in pump applications. The pressure is then prescribed at the boundaries using Bernoulli's principle,

$$p = p_{stat} = p_{tot} - \frac{1}{2}\rho|\mathbf{u}|^2 \tag{6-48}$$

The equation is imposed with two options: **Average** and **Pointwise**.

In the first option, p_{stat} is prescribed by:

$$\mathbf{n}^T(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T))\mathbf{n} = \mathbf{n}^T(-p_{stat}\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T))\mathbf{n} \tag{6-49}$$

where p_{tot} and $|\mathbf{u}|^2$ are averaged over the boundaries using the `aveop` operator:

$$p_{stat} = \mathrm{aveop}(p_{tot}) - \frac{1}{2}\rho \cdot \mathrm{aveop}(|\mathbf{u}|^2)$$

For the second option, Equation 6-48 is prescribed pointwise.

See Inlet, Outlet, Open Boundary, and No Viscous Stress for the individual node settings. Note that some modules have additional theory sections describing options available with that module.

Porous Interface

This condition properly accounts for a sudden jump in porosity ε_p across boundary between different domains, giving the corresponding jump in stress across the interface. The emergence of a boundary layer on the upstream side of the interface is also revealed, which provides modifications to the behavior of the tangential velocity near the interface. The feature helps to avoid the need to add a very thin transition region, in which $\varepsilon_{p,\mathrm{upstream}}$ changes to $\varepsilon_{p,\mathrm{downstream}}$ continuously, while solving the Brinkman equation in such situations. Below, '−' and '+' (used as subscripts and superscripts) refer to the upstream and downstream side of the interface, respectively.

Whatever the option for **Continuity conditions** is chosen, the velocity conditions are

$$[\rho(\mathbf{u} \cdot \mathbf{n})]\big|_-^+ = 0, \qquad \mathbf{u}_t\big|_-^+ \equiv [\mathbf{u} - (\mathbf{u} \cdot \mathbf{n})\mathbf{n}]\big|_-^+ = 0$$

That is, the mass flux and tangential velocity across the interface are constant, and $\mathbf{n}$ is assumed to be a normal pointing from '−' to '+'. **Velocity and stress** option just imposes usual stress continuity adding a correction for a possible jump in density:

$$\left[p\mathbf{n} - \mathbf{Kn} + \rho(\mathbf{u} \cdot \mathbf{n})\left(\left[\frac{1}{\varepsilon_p}\right]_{av}\right)^2 \mathbf{u}\right]\Bigg|_{-}^{+} = 0$$

The option **Velocity and porosity-corrected stress** (default) adds a contribution due to the inertial term, which is non-trivial (gives non-zero effect) when ε_p jumps across the interface:

$$\left[p\mathbf{n} - \mathbf{Kn} + \rho(\mathbf{u} \cdot \mathbf{n})\left(\left[\frac{1}{\varepsilon_p}\right]_{av}\right)^2 \mathbf{u} + \rho(\mathbf{u} \cdot \mathbf{n})\left(\frac{1}{2\varepsilon_p^2}\right)\mathbf{u}_{av}\right]\Bigg|_{-}^{+} = 0$$

Notice that $\left[\dfrac{1}{\varepsilon_p}\right]_{av} = \left(\left[\dfrac{1}{\varepsilon_p}\right]_{-} + \left[\dfrac{1}{\varepsilon_p}\right]_{+}\right)/2,\quad \mathbf{u}_{av} = (\mathbf{u}_{-} + \mathbf{u}_{+})/2$ and so on.

Then, the **Velocity and porosity-corrected stress with loss** option has a 'pressure loss' term:

$$\left[p\mathbf{n} - \mathbf{Kn} + \rho(\mathbf{u} \cdot \mathbf{n})\left(\left[\frac{1}{\varepsilon_p}\right]_{av}\right)^2 \mathbf{u} + \rho(\mathbf{u} \cdot \mathbf{n})\left(\frac{1}{2\varepsilon_p^2}\right)\mathbf{u}_{av}\right]\Bigg|_{-}^{+} + p^{(loss)}\mathbf{n} = 0$$

This loss occurs in the downstream direction. Its mechanism is similar to the mechanism of common engineering 'total pressure loss'. Indeed, 'expansion' and 'contraction' across the interface experienced by the flow on the microscopic level (due to increasing or decreasing porosity, ε_p, respectively), are roughly equivalent to expansion and contraction of flow in a pipe with geometrical variations. Accordingly, it is assumed that only the normal velocity component is responsible for the loss. In the case of normal flow and negligible viscous term the pipe-analogy is quite exact.

Subsequently, **Pressure loss model** should be specified. Choosing **User-defined loss coefficients** requires values of **Expansion loss coefficient** and **Contraction loss coefficient** ($K_{exp} = 1$ and $K_{contr} = 0.5$ are default values). The resulting losses on the 'expansion' and 'contraction' boundaries are:

$$p^{(\text{loss,expansion})} \;=\; K_{\text{exp}}\!\left(\!\left(\frac{\rho(\mathbf{u}\cdot\mathbf{n})^2}{2\varepsilon_p^2}\right)_{\!-}\right),$$

$$p^{(\text{loss,contraction})} \;=\; K_{\text{contr}}\!\left(\frac{\rho(\mathbf{u}\cdot\mathbf{n})^2}{2\varepsilon_p^2}\right)_{\!+}$$

Borda–Carnot option results in the following losses:

$$p^{(\text{loss,expansion})} \;=\; \frac{\rho_{\text{av}}}{2}\!\left(\left[\frac{(\mathbf{u}\cdot\mathbf{n})}{\varepsilon_p}\right]_{\!+} - \left[\frac{(\mathbf{u}\cdot\mathbf{n})}{\varepsilon_p}\right]_{\!-}\right)^{\!2},$$

$$p^{(\text{loss,contraction})} \;=\; \frac{1}{2}\!\left(\frac{\rho(\mathbf{u}\cdot\mathbf{n})^2}{\varepsilon_p^2}\right)_{\!+}\left(\frac{1}{c_{\text{vc}}}-1\right)^{\!2}$$

and requires to choose **Vena contracta model**. The **User defined** option asks for value of **Vena contracta coefficient** ($c_{\text{vc}} = 0.5$ by default). **Weisbach** option computes the coefficient based on the ratio of porosities across the interface:

$$c_{\text{vc}} \;=\; c_{\text{vc,ll}} + (1 - c_{\text{vc,ll}})\!\left(\frac{\varepsilon_{p,+}}{\varepsilon_{p,-}}\right)^{\!n_{\text{vc}}}$$

and requires inputs for **Lower limit** and **Exponent** ($c_{\text{vc,ll}} = 0.63$ and $n_{\text{vc}} = 3$ are default values).

Although the velocity conditions formally look the same for all **Continuity conditions** options, the latter two (containing the inertial correction due to the porosity jump) lead to an extra non-trivial effect. Namely, the tangential velocity exponentially evolves over a boundary layer formed on the upstream side of the interface boundary. This boundary layer has a characteristic length equal to

$$l_- \;=\; \frac{\mu\varepsilon_{p,-}}{\rho(\mathbf{u}\cdot\mathbf{n})}$$

The ratio of the tangential velocities right after the interface ('downstream') and outside the boundary layer ('upstream infinity') is

$$\frac{\left|\mathbf{u}_{t,+}\right|}{\left|\mathbf{u}_{t,\text{upstream infinity}}\right|} \;=\; \frac{2\varepsilon_{p,+}/\varepsilon_{p,-}}{\varepsilon_{p,+}/\varepsilon_{p,-} + \varepsilon_{p,-}/\varepsilon_{p,+}}$$

In terms of the interstitial velocity, $\mathbf{u}^{(i)} = \mathbf{u}/\varepsilon_p$, this results in:

$$\frac{\left|\mathbf{u}^{(i)}_{t,+}\right|}{\left|\mathbf{u}^{(i)}_{t,\text{upstream infinity}}\right|} = \frac{2}{\varepsilon_{p,+}/\varepsilon_{p,-} + \varepsilon_{p,-}/\varepsilon_{p,+}} \leq 1$$

Obviously, tangential component of the interstitial kinetic energy is lost across the interface. For low viscosity and high normal-flow component, when l_u is much lower than l_{geom} (the characteristic geometry length) there are apparent variations in $\mathbf{u}_t$ and $\mathbf{u}^{(i)}_t$ in a thin boundary layer on the upstream side of the interface. However, for the cases with high viscosity or nearly interface-parallel flow, l_u is much larger than l_{geom}, and any variations in $\mathbf{u}_t$ and $\mathbf{u}^{(i)}_t$ are virtually invisible.

Notice that the feature does not take into account possible underresolved porous scale, as is described in Theory for the Free and Porous Media Flow, Darcy Interface.

Mass Sources for Fluid Flow

There are two types of mass sources in a Single-Phase Flow interface: point sources and line sources.

	These features require at least one of the following licenses: Battery Design Module, CFD Module, Chemical Reaction Engineering Module, Corrosion Module, Electrochemistry Module, Electrodeposition Module, Fuel Cell & Electrolyzer Module, Microfluidics Module, Pipe Flow Module, Polymer Flow Module, or Subsurface Flow Module.

POINT SOURCE

A point source is theoretically formed by taking a mass injection/ejection, $\dot{Q}$ (SI unit: kg/(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, $\dot{q}_p$ (SI unit: kg/s), this can be expressed as

$$\lim_{\delta V \to 0} \int_{\delta V} \dot{Q} = \dot{q}_p \tag{6-50}$$

An alternative way to form a point source/sink 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 volume, such as drag and fluid displacement, need to be neglected.

The weak contribution

$$\dot{q}_p \text{test}(p)$$

is added to a point in the geometry. As can be seen from Equation 6-50, $\dot{Q}$ must tend to plus or minus infinity as δV tends to zero. This means that in theory the pressure 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 6-50 corresponds to a finite pressure in 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 pressure value. It is important not to mesh too finely around a point source since the resulting pressure can result in unphysical values for the density, for example. 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 $\dot{Q}$ (SI unit: $kg/(m^3 \cdot s)$), located within a tube with cross-sectional area δS and then letting δS tend to zero, while keeping the total mass flux per unit length constant. Given a line source strength, $\dot{q}_l$ (SI unit: $kg/(m \cdot s)$), this can be expressed as

$$\lim_{\delta S \to 0} \int_{\delta S} \dot{Q} = \dot{q}_l \qquad (6\text{-}51)$$

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 on the fluid resulting from the physical object volume are neglected.

The weak contribution

$$\dot{q}_l \text{test}(p)$$

is added to lines in 3D or to points in 2D (which represent cut-through views of lines). Line sources can also be added to the axisymmetry line in 2D axisymmetry

components. It cannot, however, be added to geometrical lines in 2D because they 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**).

Numerical Stability — Stabilization Techniques for Fluid Flow

The momentum equation (Equation 6-32 or Equation 6-34) is a (nonlinear) convection-diffusion equation. Such equations can easily become unstable if discretized using the Galerkin finite element method. Stabilized finite element methods are usually necessary in order to obtain physical solutions. The stabilization settings are found in the main Fluid Flow interface features. To display this section, click the **Show More Options** button (👁) and select **Stabilization** in the **Show More Options** dialog box.

There are three types of stabilization methods available for Navier–Stokes — *streamline diffusion*, *crosswind diffusion*, and *isotropic diffusion*. Streamline diffusion and crosswind diffusion are consistent stabilization methods, whereas isotropic diffusion is an inconsistent stabilization method.

For optimal functionality, the exact weak formulations of and constants in the streamline diffusion and crosswind diffusion methods depend on the order of the shape functions (basis functions) for the elements. The values of constants in the streamline diffusion and crosswind diffusion methods follow Ref. 5 and Ref. 6.

STREAMLINE DIFFUSION

For strongly coupled systems of equations, the streamline diffusion method must be applied to the system as a whole rather than to each equation separately. These ideas were first explored by Hughes and Mallet (Ref. 8) and were later extended to Galerkin least-squares (GLS) applied to the Navier–Stokes equations (Ref. 9). This is the streamline diffusion formulation that COMSOL Multiphysics supports.

Streamline diffusion is active by default because it is necessary when convection is dominating the flow.

The governing equations for incompressible flow are subject to the Babuška–Brezzi condition, which states that the shape functions (basis functions) for pressure must be of lower order than the shape functions for velocity. If the incompressible Navier–Stokes equations are stabilized by streamline diffusion, it is possible to use equal-order interpolation. Hence, streamline diffusion is necessary when using first-order elements for both velocity and pressure. This applies also if the model is solved using geometric multigrid (either as a solver or as a preconditioner) and at least one multigrid hierarchy level uses linear Lagrange elements.

CROSSWIND DIFFUSION

Crosswind diffusion can also be formulated for systems of equations, and when applied to the Navier–Stokes equations it becomes a shock-capturing operator. COMSOL Multiphysics supports the formulation in Ref. 9 with a shock-capturing viscosity of the Hughes–Mallet type Ref. 8.

Incompressible flows do not contain shock waves, but crosswind diffusion is still useful for introducing extra diffusion in sharp boundary layers and shear layers that otherwise would require a very fine mesh to resolve.

Crosswind diffusion is active by default as it makes it easier to obtain a solution even if the problem is fully resolved by the mesh. Crosswind diffusion also enables the iterative solvers to use inexpensive presmoothers. If crosswind diffusion is deactivated, more expensive preconditioners must be used instead.

STABILIZATION TIME SCALES

The time-scale tensor for time-dependent problems should in theory depend on a time-scale that many references just set to the time-step taken by the time-solver, Δt (see, for example, Ref. 9 and Ref. 10). This simple approach does not, however, necessarily reflect on the actual time-scales in the physics. A typical example is reacting flows where the time step is often guided by fast reactions, while the flow develops relatively slowly. The COMSOL Multiphysics software can therefore replace Δt^2 in the

time-scale tensor with measures of type $(1/(\Delta \tilde{t})^2)^{-1}$, which are calculated from projections of weak expressions in a fashion similar to those in Ref. 11. These measures of the time scale are used when **Use dynamic subgrid time scale** is activated.

The **Limit small time steps effect on stabilization time scale** option can be used to ramp down the time-step contribution in the stabilization when the time step becomes much smaller than the convective and diffusive time scales. This option prevents loss of pressure stabilization at such small time steps.

ISOTROPIC DIFFUSION

Isotropic diffusion adds diffusion to the Navier–Stokes equations. Isotropic diffusion significantly reduces the accuracy of the solution but does a very good job at reducing oscillations. The stability of the continuity equation is not improved.

Q | Numerical Stabilization and Iterative

Solvers for Laminar Flow

The Navier–Stokes equations constitute a nonlinear equation system. A nonlinear solver must hence be applied to solve the problem. The nonlinear solver iterates to reach the final solution. In each iteration, a linearized version of the nonlinear system is solved using a linear solver. In the time-dependent case, a time marching method must also be applied. The default suggestions for each of these solver elements are discussed below.

NONLINEAR SOLVER

The nonlinear solver method depends on if the model solves a stationary or a time-dependent problem.

Stationary Solver

In the stationary case, a fully coupled, damped Newton method is applied. The initial damping factor is low since a full Newton step can be harmful unless the initial values are close to the final solution. The nonlinear solver algorithm automatically regulates the damping factor in order to reach a converged solution.

For advanced models, the automatically damped Newton method might not be robust enough. A pseudo time-stepping algorithm can then be invoked. See Pseudo Time Stepping for Laminar Flow Models.

Time-Dependent Solver

In the time-dependent case, the initial guess for each time step is (loosely speaking) the previous time step, which is a very good initial value for the nonlinear solver. The automatic damping algorithm is then not necessary. The damping factor in the Newton method is instead set to a constant value slightly smaller than one. Also, for the same reason, it suffices to update the Jacobian once per time step.

It is seldom worth the extra computational cost to update the Jacobian more than once per time step. For most models it is more efficient to restrict the maximum time step or possibly lower the damping factor in the Newton method.

LINEAR SOLVER

The linearized Navier–Stokes equation system has saddle point character, unless the density depends on the pressure. This means that the Jacobian matrix has zeros on the diagonal. Even when the density depends on the pressure, the equation system effectively shares many numerical properties with a saddle point system.

For small 2D and 3D models, the default solver suggestion is a direct solver. Direct solvers can handle most nonsingular systems and are very robust and also very fast for small models. Unfortunately, they become slow for large models and their memory requirement scales as somewhere between $N^{1.5}$ and N^2, where N is the number of degrees of freedom in the model. The default suggestion for large 2D and 3D models is therefore the iterative GMRES solver. The memory requirement for an iterative solver optimally scales as N.

GMRES is accelerated by a multigrid method, per default the smoothed aggregation algebraic multigrid (SAAMG) method. The cost of SAAMG is typically very low compared to the number of GMRES iterations necessary if no multigrid method is used. As the name implies, SAAMG builds its coarser meshes algebraically, so the application requires no additional meshes in order to employ SAAMG. In contrast, the geometric multigrid (GMG) method requires actual meshes. If a sufficient number of multigrid levels can be constructed, GMG is often faster than SAAMG. GMG is also superior for cluster computations and for shared-memory computations with many cores. When the default linear solver is GMRES, an optional, but deactivated, linear solver node is available where GMRES is accelerated by GMG.

Multigrid methods need smoothers, but the saddle point character of the linear system restricts the number of applicable smoothers. The choices are further restricted by the anisotropic meshes frequently encountered in fluid-flow problems. The efficiency of the smoothers is highly dependent on the numerical stabilization. Iterative solvers

perform at their best when both Streamline Diffusion and Crosswind Diffusion are active.

The default smoother for P1+P1 elements is SCGS. This is an efficient and robust smoother specially designed to solve saddle point systems on meshes that contain anisotropic elements. The SCGS smoother works well even without crosswind diffusion. SCGS can sometimes work for higher-order elements, especially if **Method** in the SCGS settings is set to **Mesh element lines**. But there is no guarantee for this, so the default smoother for higher order elements is an SOR Line smoother. SOR Line handles mesh anisotropy but does not formally address the saddle point character. It does, however, function in practice provided that streamline diffusion and crosswind diffusion are both active.

A different kind of saddle point character can arise if the equation system contains ODE variables. Some advanced boundary conditions can add equations with such variables. These variables must be treated with the Vanka algorithm. SCGS includes an option to invoke Vanka. Models with higher-order elements must apply SCGS or use the Vanka smoother. The latter is the default suggestion for higher-order elements, but it does not work optimally for anisotropic meshes.

TIME-DEPENDENT SOLVERS

The default time-dependent solver for Navier–Stokes is the BDF method with maximum order set to two. Higher BDF orders are not stable for transport problems in general nor for Navier–Stokes in particular.

BDF methods have been used for a long time and are known for their stability. However, they can have severe damping effects, especially the lower-order methods. Hence, if robustness is not an issue, a model can benefit from using the generalized-α method instead. Generalized-α is a solver that has properties similar to those of the second-order BDF solver but it is much less diffusive.

Both BDF and generalized-α are per default set to automatically adjust the time step. While this works well for many models, extra efficiency and accuracy can often be gained by specifying a maximum time step. It is also often beneficial to specify an initial time step to make the solver progress smoothly in the beginning of the time series.

	• Time-Dependent Solver
⊕	• Multigrid, Direct, Iterative, SCGS, SOR Line, and Vanka
	• Stationary Solver

Pseudo Time Stepping for Laminar Flow Models

A stationary formulation has per definition no time derivatives and Equation 6-34 reduces to:

$$\rho(\mathbf{u} \cdot \nabla)\mathbf{u} \ = \ \nabla \cdot [-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T)] + \mathbf{F} \qquad (6\text{-}52)$$

Solving Equation 6-52 requires a starting guess that is close enough to the final solution. If no such guess is at hand, the fully transient problem can be solved instead. This is, however, a rather costly approach in terms of computational time. An intermediate approach is to add a fictitious time derivative to Equation 6-52:

$$\rho\frac{\mathbf{u} - \mathrm{nojac}(\mathbf{u})}{\Delta \tilde{t}} + \rho(\mathbf{u} \cdot \nabla)\mathbf{u} \ = \ \nabla \cdot [-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T)] + \mathbf{F}$$

where $\Delta \tilde{t}$ is a *pseudo time step*. Since $\mathbf{u}-\mathrm{nojac}(\mathbf{u})$ 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 step of size $\Delta \tilde{t}$ of a time-dependent solver.

Pseudo time stepping is not active per default. The pseudo time step $\Delta \tilde{t}$ can be chosen individually for each element based on the local CFL number:

$$\Delta \tilde{t} \ = \ \mathrm{CFL}_{\mathrm{loc}}\frac{h}{|\mathbf{u}|}$$

where h is the mesh cell size. A small CFL number means a small time step. It is practical to start with a small CFL number and gradually increase it as the solution approaches steady state.

If the automatic expression for $\mathrm{CFL}_{\mathrm{loc}}$ is set to the built-in variable `CFLCMP`, then the automatic setting suggests a PID regulator for the pseudo time step in the default solver. The PID regulator starts with a small CFL number and increases $\mathrm{CFL}_{\mathrm{loc}}$ as the solution comes closer to convergence.

The default manual expression is

$$\begin{aligned}
1.3^{\min(\mathrm{niterCMP},\, 9)} + & \\
\mathrm{if}(\mathrm{niterCMP} > 20,\, 9 \cdot 1.3^{\min(\mathrm{niterCMP}-20,\, 9)},\, 0) + & \\
\mathrm{if}(\mathrm{niterCMP} > 40,\, 90 \cdot 1.3^{\min(\mathrm{niterCMP}-40,\, 9)},\, 0) &
\end{aligned} \qquad (6\text{-}53)$$

The variable `niterCMP` is the nonlinear iteration number. It is equal to one for the first nonlinear iteration. $\mathrm{CFL}_{\mathrm{loc}}$ starts at 1.3 and increases by 30% each iteration until it

reaches $1.3^9 \approx 10.6$. It remains there until iteration number 20 at which it starts to increase until it reaches approximately 106. A final increase after iteration number 40 then takes it to 1060. Equation 6-53 can, for some advanced flows, increase CFL_{loc} too slowly or too quickly. CFL_{loc} can then be tuned for the specific application.

🔍 For details about the CFL regulator, see Pseudo Time Stepping.

Nitsche Constraints

Some boundary conditions are implemented using Nitsche constraints. These boundary conditions include

- Wall — Slip, sliding walls, and moving walls (that is, walls with nonzero translational velocity).
- Periodic Flow Condition
- Flow Continuity

The formulation used in the Fluid Flow interfaces in single-phase flow interfaces corresponds to the Symmetric Interior Penalty Galerkin method (SIPG). The SIPG method can be regarded to satisfy the boundary conditions in an integral sense rather than pointwise. More information on SIPG can be found in Ref. 15.

In particular, the SIPG formulation includes a penalty parameter that must be large enough for the formulation to be coercive. The higher the value, the better the boundary condition is fulfilled, but a too high value results in an ill-conditioned equation system. The penalty parameter is implemented according to Ref. 16.

Particle Tracing in Fluid Flow

The Particle Tracing Module is available to assist with these types of modeling problems.

It is possible to model particle tracing with COMSOL Multiphysics provided that the impact of the particles on the flow field is negligible. First compute the flow field, and then, as an analysis step, calculate the motion of the particles. The motion of a particle is defined by Newton's second law

$$m\frac{d^2\mathbf{x}}{dt^2} = \mathbf{F}\left(t, \mathbf{x}, \frac{d\mathbf{x}}{dt}\right)$$

where $\mathbf{x}$ is the position of the particle, m the particle mass, and $\mathbf{F}$ is the sum of all forces acting on the particle. Examples of forces acting on a particle in a fluid are the drag force, the buoyancy force, and the gravity force. The drag force represents the force that a fluid exerts on a particle due to a difference in velocity between the fluid and the particle. It includes the viscous drag, the added mass, and the Basset history term. Several empirical expressions have been suggested for the drag force. One of those is the one proposed by Khan and Richardson (Ref. 13). That expression is valid for spherical particles for a wide range of particle Reynolds numbers. The particle Reynolds number is defined as

$$\mathrm{Re}_p = \frac{|\mathbf{u} - \mathbf{u}_p| 2r\rho}{\mu}$$

where $\mathbf{u}$ is the velocity of the fluid, $\mathbf{u}_p$ the particle velocity, r the particle radius, ρ the fluid density, and μ the dynamic viscosity of the fluid. The empirical expression for the drag force according to Khan and Richardson is

$$\mathbf{F} = \pi r^2 \rho |\mathbf{u} - \mathbf{u}_p| (\mathbf{u} - \mathbf{u}_p)[1.84\,\mathrm{Re}_p^{-0.31} + 0.293\,\mathrm{Re}_p^{0.06}\,]^{3.45}$$

The model *Flow Past a Cylinder* (Application Library path **COMSOL_Multiphysics/Fluid_Dynamics/cylinder_flow**) demonstrates how to add and set up particle tracing in a plot group using the **Particle Tracing with Mass** node. It uses the predefined Khan–Richardson model for the drag force and neglects gravity and buoyancy forces.

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Theory for the Darcy's Law Interface

The Darcy's Law Interface theory is described in this section:

- About Darcy's Law
- Darcy's Law — Equation Formulation
- Storage Models
- Average Linear Velocity
- Dual Porosity and Dual Permeability Theory
- References for the Darcy's Law Interface

About Darcy's Law

In a porous medium, the global transport of momentum by shear stresses in the fluid is often negligible, because the pore walls impede momentum transport to the fluid outside the individual pores. A detailed description, down to the resolution of every pore, is not practical in most applications. A homogenization of the porous and fluid media into a single medium is a common alternative approach. Darcy's law together with the continuity equation and equation of state for the pore fluid (or gas) provide a complete mathematical model suitable for a wide variety of applications involving porous media flows, for which the pressure gradient is the major driving force.

Darcy's law describes fluid movement through interstices in a porous medium. Because the fluid loses considerable energy to frictional resistance within pores, flow velocities in porous media are very low. The Darcy's Law interface can be applied to small-scale tasks in chemical engineering as well as to large-scale geophysical or hydrological tasks such as water moving in an aquifer or stream bank, oil migrating to a well, and even magma rising through the earth to a chamber in a volcano (see Ref. 1, Ref. 2, Ref. 3, and Ref. 4). Also set up multiple Darcy's Law interfaces to model multiphase flows involving more than one mobile phase.

Darcy's law describes flow in porous media driven by gradients in the hydraulic potential field, which has units of pressure. For many applications it is convenient to represent the total hydraulic potential or the pressure and the gravitational components with equivalent heights of fluid or head. Division of potential by the fluid weight can simplify modeling because units of length make it straightforward to compare to many physical data. Consider, for example, fluid levels in wells, stream heights, topography, and velocities. The physics interface also supports specifying

boundary conditions and result evaluation using hydraulic head and pressure head. In the physics interface, pressure is always the dependent variable.

Darcy's Law — Equation Formulation

Darcy's law states that the velocity field is determined by the pressure gradient, the fluid viscosity, and the structure of the porous medium:

$$\mathbf{u} = -\frac{\kappa}{\mu}\nabla p \tag{6-54}$$

In this equation, $\mathbf{u}$ is the Darcy's velocity or specific discharge vector (SI unit: m/s); κ is the permeability of the porous medium (SI unit: m^2); μ is the fluid's dynamic viscosity (SI unit: Pa·s); p is the pore pressure (SI unit: Pa) and ρ is the density of the fluid (SI unit: kg/m^3).

📝
- The above equation formulation is called linear Darcy's law. The applicability of this formulation is discussed in the chapter About Darcian and Non-Darcian Flow in the *Porous Media Flow Module User's Guide*.
- Permeability can be defined in different ways, either directly or based on predefined permeability models. These are described in detail in the chapter Permeability Models.
- For a detailed overview of the permeability models available in each product visit https://www.comsol.com/products/specifications/.

The Darcy's Law interface combines Darcy's law with the continuity equation

$$\frac{\partial}{\partial t}(\rho\varepsilon_p) + \nabla \cdot (\rho\mathbf{u}) = Q_m \tag{6-55}$$

In the above equation, ρ is the fluid density (SI unit: kg/m^3), ε_p is the porosity, and Q_m is a mass source term (SI unit: $kg/(m^3 \cdot s)$). Porosity is defined as the fraction of the control volume that is occupied by pores. Thus, the porosity can vary from zero for pure solid regions to unity for domains of free flow.

For large-scale applications it might be necessary to take gravity effects into account. Darcy's law then applies when the gradient in hydraulic potential drives fluid movement in the porous medium. Darcy's law then has the form:

$$\mathbf{u} = -\frac{\kappa}{\mu}(\nabla p - \rho \mathbf{g}) \qquad (6\text{-}56)$$

> - See the section Gravity Effects in the *Subsurface Flow Module User's Guide*.
> - Note that gravity effects are only included in some modules. For a detailed overview of the functionality available in each product visit https://www.comsol.com/products/specifications/.
> - Gravity effects are not active by default. Select the check box **Include gravity** to activate the acceleration of gravity. Setting the elevation D to zero also turns off gravity effects.

Storage Models

The continuity equation (Equation 6-55) allows flexible specification of relationships between parameters like density or permeability with respect to variables such as pressure, temperature, concentration, and more.

Expanding the time-derivative term and defining the porosity and density as functions of the pressure and using the chain rule results in

$$\frac{\partial}{\partial t}(\rho \varepsilon_p) = \varepsilon_p \frac{\partial \rho}{\partial t} + \rho \frac{\partial \varepsilon_p}{\partial t} = \varepsilon_p \frac{\partial \rho}{\partial p}\frac{\partial p}{\partial t} + \rho \frac{\partial \varepsilon_p}{\partial p}\frac{\partial p}{\partial t}$$

By inserting the definition of fluid compressibility $\chi_f = (1/\rho)(\partial \rho / \partial p)$ to the right-hand side and rearrange the following expression is obtained

$$\frac{\partial(\rho \varepsilon_p)}{\partial t} = \rho \left(\varepsilon_p \chi_f + \frac{\partial \varepsilon_p}{\partial p} \right) \frac{\partial p}{\partial t} = \rho S_P \frac{\partial p}{\partial t}$$

Using this relation, the generalized governing equation (Equation 6-55) takes the following form:

$$\rho S_P \frac{\partial p}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = Q_m \qquad (6\text{-}57)$$

In this equation, S_p is the storage coefficient (SI unit: $1/\text{Pa}$), which can be interpreted as the weighted compressibility of the porous material and the fluid. The storage can be an expression involving results from a solid-deformation equation or an expression involving temperatures and concentrations from other analyses. The Darcy's Law

interface implements Equation 6-57 in the **Porous Medium** node, which explicitly includes different storage models to choose from:

- **From density and porosity**, where the storage directly depends on changes in porosity or fluid density

- **Linearized storage**, which defines S_p using the compressibility of the fluid χ_f and of the porous matrix χ_p according to

$$S_p = \varepsilon_p \chi_f + (1 - \varepsilon_p)\chi_p$$

- **Poroelastic storage** where

$$S_p = \varepsilon_p \chi_f .$$

📄 Storage models are only available for the Subsurface Flow Module and the Porous Media Flow Module. For a detailed overview of the functionality available in each product visit https://www.comsol.com/products/specifications/.

Average Linear Velocity

Because fluids typically occupy only 10% to 50% of a porous medium, it follows that velocities within the pore channels exceed the Darcy velocity, **u**, on the order of two to ten times. For clarity, the physics interface includes the average linear velocity within the pores, $\mathbf{u}_\alpha$, (also termed the seepage velocity) defined as $\mathbf{u}_\alpha = \mathbf{u}/\varepsilon_p$, where ε_p is the porosity.

Dual Porosity and Dual Permeability Theory

The first well known publication on this topic is "The Behavior of Naturally Fractured Reservoirs" by J.E.Warren and P.J. Root from 1963. Since then the researchers further developed the idea of a dual porosity/permeability type of a porous medium. One of the well established models is based on the findings of H. Gerke and M. van Genuchten (Ref. 9). Basically the idea behind is to solve for each part of the porous medium (macro- and micropores) the relevant equations and connect them via an exchange term.

DUAL POROSITY MEDIUM

Darcy's Law is solved for the macropores and taking into account their volume fraction θ_M the equation reads:

$$\theta_M \left(\rho S_{p,M} \frac{\partial p_M}{\partial t} + \nabla(\rho \mathbf{u}_M) \right) = \theta_M Q_M - Q_{ip} \qquad (6\text{-}58)$$

The term Q_{ip} describes the mass source from the Interporosity Flow which is the mass transfer from the macropores to the micropores system. An additional ODE for the (passive) micropores is solved which only act as additional storage volume:

$$(1 - \theta_M) \left(\rho S_{p,m} \frac{\partial p_m}{\partial t} \right) = (1 - \theta_M) Q_M + Q_{ip}.$$

The indices M and m stand for macropores and micropores, respectively.

DUAL PERMEABILITY MEDIUM

Darcy's law has to be solved for both the macroscale system and the microscale system:

$$\theta_M \left(\frac{\partial}{\partial t}(\varepsilon_{p,M} \rho) + \nabla \cdot (\rho \mathbf{u}_M) \right) = -Q_{ip} + \theta_M Q_m$$

$$(1 - \theta_M) \left(\frac{\partial}{\partial t}(\varepsilon_{p,m} \rho) + \nabla \cdot (\rho \mathbf{u}_m) \right) = Q_{ip} + (1 - \theta_M) Q_m \qquad (6\text{-}59)$$

$$p = \theta_M p_M + (1 - \theta_M) p_m$$

θ_M is the volume fraction of the macropores, Q_{ip} denotes the interporosity flow, signifying the mass transfer from the macropores (identified by index M) to the micropores (identified by index m).

Solving Darcy's law for both systems entails solving two equations, each associated with dependent pressure variables p_m and p_M. These equations are coupled via Q_{ip}. From this, average quantities for the dual permeability medium as a whole are computed. The average pressure of the dual permeability medium is defined as:

$$p = \theta_M p_M + (1 - \theta_M) p_m$$

Likewise, average values for permeability, storage, velocity and other relevant parameters are computed.

UNSATURATED DUAL PERMEABILITY MEDIUM

Use the **Unsaturated Dual Permeability Medium** feature to model the transport in an unsaturated dual permeability medium where the Richards' Equation (Equation 4-26) describes the transport in each system.

$$\theta_M\left(\rho\left(S_{e,M}S_{p,M} + \frac{C_{m,M}}{\rho g}\right)\frac{\partial p_M}{\partial t} + \nabla(\rho \mathbf{u}_M)\right) = -Q_{ip} + \theta_M Q_m$$

$$(1-\theta_M)\left(\rho\left(S_{e,m}S_{p,m} + \frac{C_{m,m}}{\rho g}\right)\frac{\partial p_m}{\partial t} + \nabla(\rho \mathbf{u}_m)\right) = Q_{ip} + (1-\theta_M)Q_m \qquad (6\text{-}60)$$

$$p = \theta_M p_M + (1-\theta_M)p_m$$

θ_M is the volume fraction of the macropores, Q_{ip} is the interporosity flow which is the mass transfer from the macroscale to the microscale system. The indices M and m stand for macropores and micropores, respectively.

INTERPOROSITY FLOW

Specify the **Fluid Transfer Function** α_w which is used to calculate the interporosity flow, which is the mass exchange between macro- and microscale system:

$$Q_{ip} = \alpha_w(p_M - p_m) \qquad (6\text{-}61)$$

with p_M being the pressure within the macroscale system and p_m the pressure within the microscale system

References for the Darcy's Law Interface

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Theory for the Free and Porous Media Flow, Brinkman Interface

The Free and Porous Media Flow, Brinkman Interface uses the Navier–Stokes equations to describe the flow in open regions, and the Brinkman equations to describe the flow in porous regions.

The same fields, $\mathbf{u}$ and p, are solved for in both the free flow domains and in the porous domains. This means that the pressure in the free fluid and the pressure in the pores is continuous over the interface between a free flow domain and a porous domain. It also means that continuity is enforced between the fluid velocity in the free flow and the Darcy velocity in the porous domain. This treatment is one of several possible models for the physics at the interface. Examples of other models can be found in Ref. 1.

The continuity in $\mathbf{u}$ and p implies a stress discontinuity at the interface between a free-flow domain and a porous domain. The difference corresponds to the stress absorbed by the rigid porous matrix, which is a consequence implicit in the formulations of the Navier–Stokes and Brinkman equations.

Reference for the Free and Porous Media Flow, Brinkman Interface

1. M.L. Bars and M.G. Worster, "Interfacial Conditions Between a Pure Fluid and a Porous Medium: Implications for Binary Alloy Solidification," *J. Fluid Mech.*, vol. 550, pp. 149–173, 2006.

Theory for the Free and Porous Media Flow, Darcy Interface

The **Free and Porous Media Flow, Darcy** interface uses the Navier–Stokes equations to describe the flow in the free-flow region, implemented by the coupled Laminar Flow interface, and Darcy's law, implemented by the coupled Darcy's Law interface, to describe the flow in the porous region.

In the free-flow region, the velocity u and pressure p are solved for, whereas in the porous region only the pressure p is solved for, and the velocity is calculated from the pressure by Darcy's law.

The coupling between the free and porous medium flow, implemented by the Free and Porous Media Flow Coupling, ensures conservation of mass across the free-porous interface, which is enforced by the condition

$$\mathbf{n} \cdot (\rho_{ns}\mathbf{u}_{ns}) = \mathbf{n} \cdot (\rho_d\mathbf{u}_d) \tag{6-62}$$

Here ρ_{ns} and $\mathbf{u}_{ns}$ are the density and velocity on the free-flow side of the interface, ρ_d and $\mathbf{u}_d$ the density and velocity on the porous side, and $\mathbf{n}$ is a vector normal to the interface. In addition the coupling enforces the balance of the normal forces by:

$$p_{ns} - \mathbf{n} \cdot \mathbf{K}\mathbf{n} = p_d \tag{6-63}$$

where p_{ns} and p_d are the pressure on the free-flow side and porous side of the interface, respectively, and $\mathbf{K}$ is the viscous stress tensor (defined only on the free-flow side).

For the coupling condition for the tangential velocity component, there are several options. One of the most widely used conditions is the **Beavers-Joseph** interface condition (Ref. 1):

$$(\mathbf{I} - \mathbf{n} \otimes \mathbf{n})(\mathbf{u}_{ns} - \mathbf{u}_d) = \frac{\sqrt{\mathrm{tr}(\kappa)/n}}{\mu_{ns}\alpha_{BJ}}(\mathbf{I} - \mathbf{n} \otimes \mathbf{n})\mathbf{K}\mathbf{n} \tag{6-64}$$

where α_{BJ} is the Beavers and Joseph parameter, κ is the permeability tensor of the porous medium (defined on the porous side of the interface), μ_{ns} is the fluid's dynamic viscosity on the free-flow side of the interface, and n is the number of space dimensions.

When the velocity in the porous domain is much smaller than the velocity in the free flow, one can use a modification of the Beavers–Joseph condition which is given by the **Beavers–Joseph–Saffman** interface condition (Ref. 2):

$$(\mathbf{I} - \mathbf{n} \otimes \mathbf{n})\mathbf{u}_{ns} = \frac{\sqrt{\mathrm{tr}(\kappa)/n}}{\mu_{ns}\alpha_{BJ}}(\mathbf{I} - \mathbf{n} \otimes \mathbf{n})\mathbf{Kn} \qquad (6\text{-}65)$$

For cases when the permeability tensor is not isotropic, the **Use projected permeability** option allows to take into account only the permeability in the direction of the tangential velocity component. This is accomplished by replacing the $\sqrt{\mathrm{tr}(\kappa)/n}$ term on the rights hand side of Equation 6-64 and Equation 6-65 by:

$$\sqrt{\mathbf{t} \cdot \kappa \mathbf{t}} \qquad (6\text{-}66)$$

with $\mathbf{t}$ a unit vector tangent to the interface for 2D and 2D-axisymmetric cases, and for 3D cases by:

$$\sqrt{\mathbf{v} \cdot \kappa \mathbf{v}} \qquad (6\text{-}67)$$

with $\mathbf{v}$ given by:

$$\mathbf{v} = \frac{(\mathbf{I} - \mathbf{n} \otimes \mathbf{n})\mathbf{Kn}}{\|(\mathbf{I} - \mathbf{n} \otimes \mathbf{n})\mathbf{Kn}\|} \qquad (6\text{-}68)$$

If one considers the limit of the Beavers–Joseph condition for large values of the Beavers and Joseph parameter a_{BJ}, one obtains the **Continuous tangential velocity** condition:

$$(\mathbf{I} - \mathbf{n} \otimes \mathbf{n})(\mathbf{u}_{ns} - \mathbf{u}_d) = 0 \qquad (6\text{-}69)$$

The same limit for the Beavers–Joseph–Saffman condition results in the **No slip** condition:

$$(\mathbf{I} - \mathbf{n} \otimes \mathbf{n})\mathbf{u}_{ns} = 0 \qquad (6\text{-}70)$$

The **Viscous slip** condition allows for a more general coupling condition. This interface condition is given by:

$$(\mathbf{I} - \mathbf{n} \otimes \mathbf{n})(\mathbf{u}_{ns} - \mathbf{u}_b) = \frac{L_s}{\mu_{ns}}(\mathbf{I} - \mathbf{n} \otimes \mathbf{n})\mathbf{Kn} \qquad (6\text{-}71)$$

Here L_s is a slip length, and $\mathbf{u}_b$ a user-defined interfacial velocity.

🔍	Please find related information in the *CFD Module User's Guide*: • The Darcy's Law Interface • The Thin-Film and Porous Media Flow Interface • The Laminar Flow Interface • Theory for the Single-Phase Flow Interfaces

References

1. G.S. Beavers and D.D. Joseph, "Boundary Conditions at a Naturally Permeable Wall," *J. Fluid Mech.*, vol. 30, 1967.

2. P.G. Saffman, "On the Boundary Condition at the Surface of a Porous Medium," *Stud. Appl. Maths*, vol. 50, 1971.

Theory for the Brinkman Equations Interface

theory is described in this section:

- About the Brinkman Equations
- Brinkman Equations Theory
- References for the Brinkman Equations Interface

About the Brinkman Equations

In porous domains, the flow variables and fluid properties are defined at any point inside the medium by means of averaging of the actual variables and properties over a certain volume surrounding the point. This control volume must be small compared to the typical macroscopic dimensions of the problem, but it must be large enough to contain many pores and solid matrix elements.

Porosity is defined as the fraction of the control volume that is occupied by pores. Thus, the porosity can vary from zero for pure solid regions to unity for domains of free flow.

The physical properties of the fluid, such as density and viscosity, are defined as *intrinsic volume averages* that correspond to a unit volume of the pores. Defined this way, they present the relevant physical parameters that can be measured experimentally, and they are assumed to be continuous with the corresponding parameters in the adjacent free flow.

The flow velocity is defined as a *superficial volume average*, and it corresponds to a unit volume of the medium including both the pores and the matrix. It is sometimes called the Darcy velocity, defined as the volume flow rate per unit cross section of the medium. Such a definition makes the velocity field continuous across the boundaries between porous regions and regions of free flow.

Brinkman Equations Theory

The dependent variables in the Brinkman equations are the Darcy velocity and the pressure. The flow in porous media is governed by a combination of the continuity equation and the momentum equation, which together form the Brinkman equations:

$$\frac{\partial}{\partial t}(\varepsilon_p \rho) + \nabla \cdot (\rho \mathbf{u}) = Q_m \qquad (6\text{-}72)$$

$$\frac{\rho}{\varepsilon_p}\left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\frac{\mathbf{u}}{\varepsilon_p}\right) =$$

$$(6\text{-}73)$$

$$-\nabla p + \nabla \cdot \left[\frac{1}{\varepsilon_p}\left\{\mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right\}\right] - \left(\kappa^{-1}\mu + \frac{Q_m}{\varepsilon_p^2}\right)\mathbf{u} + \mathbf{F}$$

In these equations:

- μ (SI unit: kg/(m·s)) is the dynamic viscosity of the fluid
- $\mathbf{u}$ (SI unit: m/s) is the velocity vector
- ρ (SI unit: kg/m^3) is the density of the fluid
- p (SI unit: Pa) is the pressure
- ε_p is the porosity
- κ (SI unit: m^2) is the permeability of the porous medium, and
- Q_m (SI unit: kg/(m^3·s)) is a mass source or sink

Influence of gravity and other volume forces can be accounted for via the force term $\mathbf{F}$ (SI unit: kg/(m^2·s^2)).

When the **Neglect inertial term (Stokes flow)** check box is selected, the term $(\mathbf{u} \cdot \nabla)(\mathbf{u}/\varepsilon_p)$ on the left-hand side of Equation 6-73 is disabled.

The mass source, Q_m, accounts for mass deposit and mass creation within the domains. The mass exchange is assumed to occur at zero velocity.

The Forchheimer and Ergun drag options add a viscous force proportional to the square of the fluid velocity, $\mathbf{F} = -\rho\beta|\mathbf{u}|\mathbf{u}$, on the right-hand side of Equation 6-73 .

In case of a flow with variable density, Equation 6-72 and Equation 6-73 must be solved together with the equation of state that relates the density to the temperature and pressure (for instance the ideal gas law).

For incompressible flow, the density stays constant in any fluid particle, which can be expressed as

$$\frac{\partial}{\partial t}(\varepsilon_p \rho) + \mathbf{u} \cdot \nabla \rho = 0$$

and the continuity equation (Equation 6-72) reduces to

$$\rho \nabla \cdot \mathbf{u} = Q_m$$

References for the Brinkman Equations Interface

1. D. Nield and A. Bejan, *Convection in Porous Media*, 3rd ed., Springer, 2006.

2. M. Le Bars and M.G. Worster, "Interfacial Conditions Between a Pure Fluid and a Porous Medium: Implications for Binary Alloy Solidification," *J. Fluid Mech.*, vol. 550, pp. 149–173, 2006.

Theory for the Multiphase Flow in Porous Media Interface

The model equations that are solved in the **Multiphase Flow in Porous Media** interface are based on the mass conservation of each phase and on an extended Darcy's law. The mass conservation equation for each phase is given by

$$\frac{\partial}{\partial t}(\varepsilon_p \rho_i s_i) + \nabla \cdot (\rho_i \mathbf{u}_i) = Q_i \tag{6-74}$$

where ε_p (dimensionless) is the porosity, and the vector $\mathbf{u}_i$ should be interpreted as the volumetric flux of phase i (SI unit $m^3/(m^2 \cdot s)$ or m/s). The volumetric fluxes are determined using the extended Darcy's law (Ref. 2)

$$\mathbf{u}_i = -\frac{\kappa_{ri}}{\mu_i}\kappa(\nabla p_i - \rho_i \mathbf{g}) \tag{6-75}$$

where κ denotes the permeability (SI unit: m^2) of the porous medium, $\mathbf{g}$ the gravitational acceleration vector (SI unit: m/s^2), and μ_i the dynamic viscosity (SI unit: kg/(m·s)), p_i the pressure field (SI unit: Pa), and κ_{ri} the relative permeability (dimensionless) of phase i, respectively. The phase pressures p_i are related through the capillary pressure functions $p_{c_{ij}}$:

$$p_i - p_j = p_{c_{ij}}(s_1, \ldots, s_N) \qquad i \neq j \tag{6-76}$$

One phase pressure can be chosen independently so that $N - 1$ capillary pressure relations are needed to define the other phase pressures. In addition it is assumed that all phases together fill the pore space completely, so that we have

$$\sum_{i=1}^{N} s_i = 1 \tag{6-77}$$

Pressure-Saturation Formulation

The algebraic relations in Equation 6-76 and Equation 6-77 allow for a reduction of the number of dependent variables. An often used way is to eliminate $N - 1$ phase pressures and one of the saturations. This results in a so-called pressure-saturation

formulation (Ref. 3). The procedure in the **Multiphase Flow in Porous Media** interface is to pick one of the phases, let us say phase i_c, then express the volume fraction, or saturation, s_{i_c}, of this phase in terms of the saturations of the other phases and in addition to use the pressure, p_{i_c}, of this phase to define the other phase pressures:

$$s_{i_c} = 1 - \left(\sum_{i=1, i \neq i_c}^{N} s_i \right) \tag{6-78}$$

$$p_i = p_{i_c} + p_{c_i}(s_1, ..., s_N) \qquad \text{for} \quad i \neq i_c \tag{6-79}$$

The equations for the saturations s_i, $(i \neq i_c)$ are given by Equation 6-74 and Equation 6-75. To arrive at an equation for p_{i_c}, the conservation equations of all phases are summed. This results in

$$\frac{\partial}{\partial t}\left(\varepsilon_p \sum_{i=1}^{N} \rho_i s_i \right) + \nabla \cdot \left(\sum_{i=1}^{N} \rho_i \mathbf{u}_i \right) = Q_{tot} \tag{6-80}$$

where the total mass source Q_{tot} is given by

$$Q_{tot} = \sum_{i=1}^{N} Q_i \tag{6-81}$$

The equations for the saturations s_i are solved in the **Phase Transport in Porous Media** interface (Equation 6-74 and Equation 6-75). The Equation 6-80 for the pressure field p_{i_c}, needed as an input to the **Phase Transport in Porous Media** interface, is solved for in the **Darcy's Law** interface: the **Multiphase Flow in Porous Media** multiphysics coupling interface replaces the equation

$$\frac{\partial}{\partial t}(\varepsilon_p \rho_{tot}) + \nabla \cdot (\rho_{tot} \mathbf{u}_d) = Q_m \quad \text{where} \quad \mathbf{u}_d = -\frac{1}{\mu}\kappa(\nabla p - \rho_{tot}\mathbf{g}) \tag{6-82}$$

which is originally implemented in the **Darcy's Law** interface, with Equation 6-80 by adding the following terms to the left-hand side of Equation 6-82:

$$\nabla \cdot \left(\sum_{i=1}^{N} \rho_i \mathbf{u}_i - \rho_{tot} \mathbf{u}_d \right) \tag{6-83}$$

and by setting the right-hand side Q_m to be equal to Q_{tot}. The volume averaged density ρ_{tot} is given by

$$\rho_{tot} = \sum_{i=1}^{N} \rho_i s_i \tag{6-84}$$

Furthermore, the **Multiphase Flow in Porous Media** multiphysics coupling interface couples the user inputs for the porosity and permeability of the porous matrix in the **Darcy's Law** interface to the corresponding user input fields in the **Phase and Porous Media Transport Properties** feature, and couples the pressure field computed for in the **Darcy's Law** interface to the user input field for the pressure of the phase computed from the volume constraint.

Note that when the hydraulic conductivity of a domain is specified in the **Darcy's Law** interface (instead of the permeability), the coupled **Phase and Porous Media Transport Properties** feature is supplied with a permeability that is computed using a reference kinematic viscosity of $1.004 * 10^{-6}$ m^{2}s^{-1} (kinematic viscosity of water at 293.15 K).

In the other direction, the multiphysics coupling node provides the averaged density (denoted by ρ_{tot} in Equation 6-83 above) and effective viscosity to the **Darcy's Law** interface.

Mass Source

When adding a Mass Source node in the coupled Phase Transport interface, it is by default assumed that the net mass source of all phases, Q_{tot}, equals zero. This implies

$$Q_{i_c} = - \sum_{i=1, i \neq i_c}^{N} Q_i \tag{6-85}$$

However, when mass is transferred from or to phases not accounted for in the phase transport interface — for instance, when mass is released or absorbed by the solid part of the porous matrix — select the **Mass transfer to other phases** check box. In this case the mass source for the phase calculated from the volume constraint should also be specified, and the net total mass source Q_{tot} is supplied as a right-hand side to the Darcy Equation 6-80 for p_{i_c}.

Boundary Conditions

When supplying boundary conditions for the coupled **Phase Transport in Porous Media** and **Darcy's Law** interfaces, bear in mind that the **Pressure** boundary condition in the **Darcy's Law** interface affects the pressure of the phase from the volume constraint, p_{i_c}. If the pressure of another phase needs to supplied, then take into account the capillary pressure.

Since the coupled **Darcy's Law** interface uses the conservation equation for the total mass (Equation 6-80) to solve for p_{i_c}, the **Mass Flux** boundary condition in the **Darcy's Law** interface should be used to prescribe the mass flux of all phases together.

If the mass flux of the phase computed from the volume constraint needs to be prescribed at a boundary, and the total mass flux is not known a priori, it might be necessary to compute for the total mass flux in the form of a Lagrange multiplier by using the weak constraint formulation for the pressure boundary condition in the **Darcy's Law** interface.

Thin Barrier (Multiphysics Coupling)

The **Thin Barrier** multiphysics coupling uses the Extra Dimension tool to solve the equations for the pressure and saturations through the thin barrier structure's thickness. The thin structure has its domain represented by the product space between the lumped boundary and the additional dimension for the thickness. Inside this product space, it is convenient to split the gradient operator into a tangential part and a normal part: $\nabla = \nabla_{\mathbf{t}} + \nabla_{\mathbf{n}}$.

The following assumptions, used in deriving the **Thin Barrier** equations from the equations solved in the **Multiphase Flow in Porous Media** interface, justify the simplification $\nabla = \nabla_{\mathbf{n}}$:

- A thin barrier can be considered as a boundary of thickness significantly smaller than the typical lengths of the overall model.

- The permeability of the porous material inside the thin barrier is significantly smaller than the permeability of the porous material in the adjacent domains.

- There is no mass source or sink inside the thin barrier.

In addition, these assumptions imply that the effect of gravity on the phase transport can be neglected. This results in the following set of equations for the saturations s_i, ($i \neq i_c$) and the pressure p_{i_c}:

$$\frac{\partial}{\partial t}(\varepsilon_\mathrm{p}\rho_i s_i) + \nabla_\mathbf{n} \cdot (\rho_i \mathbf{u}_i) = 0 \quad \text{for} \quad i \neq i_c \tag{6-86}$$

$$\mathbf{u}_i = -\frac{\kappa_{\mathrm{r}i}}{\mu_i}\kappa\nabla_\mathbf{n} p_i \tag{6-87}$$

$$\frac{\partial}{\partial t}\left(\varepsilon_\mathrm{p}\sum_{i=1}^{N}\rho_i s_i\right) + \nabla_\mathbf{n} \cdot \left(\sum_{i=1}^{N}\rho_i \mathbf{u}_i\right) = 0 \tag{6-88}$$

Together with the algebraic relations

$$s_{i_c} = 1 - \left(\sum_{i=1, i \neq i_c}^{N} s_i\right) \tag{6-89}$$

$$p_i = p_{i_c} + p_{c_i}(s_1, ..., s_N) \qquad \text{for} \quad i \neq i_c \tag{6-90}$$

Here ε_p (dimensionless) denotes the porosity and κ the permeability (SI unit: m^2) of the porous material in the thin barrier. Further more ρ_i denotes the density (SI unit: kg/m^3), μ_i the dynamic viscosity (SI unit: kg/(m·s)), p_i the pressure field (SI unit: Pa), $\mathbf{u}_i$ the (normal) volumetric flux (SI unit: m/s) and $\kappa_{\mathrm{r}i}$ the relative permeability (dimensionless) of phase i, respectively.

Since the interfaces between the thin barrier and the adjacent domains are boundaries between a more permeable and a less permeable porous domain, conditions analogous to the Porous Medium Discontinuity Boundary Condition are needed to couple the equation Equation 6-86 for the saturations inside the thin barrier to the equations in the adjacent domains. These condition at the extremities of the extra dimension can be written as:

$$p_{c_i}^t(s_i^t)_{L=0} = \begin{cases} p_{\mathrm{ec},i}^t & \text{if} \quad p_{c_i}^d(s_i^d) \leq p_{\mathrm{ec},i}^t \\ p_{c_i}^d(s_i^d) & \text{if} \quad p_{c_i}^d(s_i^d) > p_{\mathrm{ec},i}^t \end{cases} \qquad \text{for} \quad i \neq i_c \tag{6-91}$$

where the superscript t is used to indicate the saturation and capillary pressure inside the thin barrier (the low permeable side of the interface), and the superscript d indicates the domain adjacent to the downside of the thin barrier (the high permeable side), and

$$p_{c_i}^t(s_i^t)_{L=d_s} = \begin{cases} p_{ec,i}^t & \text{if} & p_{c_i}^u(s_i^u) \leq p_{ec,i}^t \\ p_{c_i}^u(s_i^u) & \text{if} & p_{c_i}^u(s_i^u) > p_{ec,i}^t \end{cases} \quad \text{for} \quad i \neq i_c \qquad (6\text{-}92)$$

where the superscript u indicates the domain adjacent to the upside of the thin barrier (again the high permeable side) and where d_s is the length of the extra dimension, or equivalently, the thickness of the thin structure.

The additional conditions are continuity of the fluxes for all phases and continuity of the pressure of the phase i_c computed from the volume constraint. Note that this last condition assumes that this phase is present both inside the thin barrier and in the adjacent domains. Furthermore, this boundary condition assumes that the phase i_c computed from the volume constraint is the wetting phase and it is necessary that the settings for the van Genuchten or Brooks and Corey capillary pressure model in the adjacent domains match this assumption.

Please find related information under

- Theory for the Phase Transport Interfaces in the *CFD Module User's Guide* and

- Using Extra Dimensions in the *COMSOL Multiphysics Reference Manual*.

References

1. J. Bear, *Dynamics of Fluids in Porous Media*, Elsevier Scientific Publishing, 1972.

2. Z. Chen, G. Huan, and Y. Ma, *Computational Methods for Multiphase Flows in Porous Media*, Philadelphia: Society for Industrial and Applied Mathematics, 2006.

3. R. Helmig, *Multiphase Flow and Transport Processes in the Subsurface − A Contribution to the Modeling of Hydrosystems*, Springer–Verlag, 1997.

Theory for the Bubbly Flow Interface

The Bubbly Flow interfaces are suitable for macroscopic modeling of mixtures of liquids and gas bubbles. These physics interfaces solve for the averaged volume fraction occupied by each of the two phases, rather than tracking each bubble in detail. Each phase has its own velocity field.

In this section:

- The Bubbly Flow Equations
- Turbulence Modeling in Bubbly Flow Applications
- References for the Bubbly Flow Interfaces

The Bubbly Flow Equations

The two-fluid Euler–Euler Model is a general, macroscopic model for two-phase fluid flow. It treats the two phases as interpenetrating media, tracking the averaged concentration of the phases. One velocity field is associated with each phase. A momentum balance equation and a continuity equation describe the dynamics of each of the phases. The *bubbly flow* model is a simplification of the two-fluid model, relying on the following assumptions:

- The gas density is negligible compared to the liquid density.
- The motion of the gas bubbles relative to the liquid is determined by a balance between viscous drag and pressure forces.
- The two phases share the same pressure field.

Based on these assumptions, the momentum and continuity equations for the two phases can be combined and a gas phase transport equation is kept in order to track the volume fraction of the bubbles. The momentum equation is

$$
\phi_1 \rho_1 \frac{\partial \mathbf{u}_1}{\partial t} + \phi_1 \rho_1 \mathbf{u}_1 \cdot \nabla \mathbf{u}_1 =
$$
$$
= -\nabla p + \nabla \cdot \left[\phi_1 (\mu_1 + \mu_T) \left(\nabla \mathbf{u}_1 + \nabla \mathbf{u}_1^T - \frac{2}{3} (\nabla \cdot \mathbf{u}_1) \mathbf{I} \right) \right] + \phi_1 \rho_1 \mathbf{g} + \mathbf{F}
$$

(6-93)

In Equation 6-93, the variables are as follows:

- $\mathbf{u}_1$ is the velocity vector (SI unit: m/s)

- p is the pressure (SI unit: Pa)
- ϕ is the phase volume fraction (SI unit: m^3/m^3)
- ρ is the density (SI unit: kg/m^3)
- $\mathbf{g}$ is the gravity vector (SI unit: m/s^2)
- $\mathbf{F}$ is any additional volume force (SI unit: N/m^3)
- μ_l is the dynamic viscosity of the liquid (SI unit: Pa·s), and
- μ_T is the turbulent viscosity (SI unit: Pa·s)

The subscripts "l" and "g" denote quantities related to the liquid phase and the gas phase, respectively.

The continuity equation is

$$\frac{\partial}{\partial t}(\rho_l \phi_l + \rho_g \phi_g) + \nabla \cdot (\rho_l \phi_l \mathbf{u}_l + \rho_g \phi_g \mathbf{u}_g) = 0 \qquad (6\text{-}94)$$

and the gas phase transport equation is

$$\frac{\partial \rho_g \phi_g}{\partial t} + \nabla \cdot (\phi_g \rho_g \mathbf{u}_g) = -m_{gl} \qquad (6\text{-}95)$$

where m_{gl} is the mass transfer rate from the gas to the liquid (SI unit: $kg/(m^3 \cdot s)$).

For low gas volume fractions ($\phi_g \sim 0.01$), you can replace the momentum equations, Equation 6-93, and the continuity equation, Equation 6-94, by

$$\rho_l \frac{\partial \mathbf{u}_l}{\partial t} + \rho_l \mathbf{u}_l \cdot \nabla \mathbf{u}_l = \qquad (6\text{-}96)$$

$$= -\nabla p + \nabla \cdot [(\mu_l + \mu_T)(\nabla \mathbf{u}_l + \nabla \mathbf{u}_l^T)] + \phi_l \rho_l \mathbf{g} + \mathbf{F}$$

$$\rho_l \nabla \cdot \mathbf{u}_l = 0 \qquad (6\text{-}97)$$

By default, the Laminar Bubbly Flow interface uses Equation 6-96 and 6-97. To switch to Equation 6-93 and 6-94, click to clear the **Low gas concentration** check box under the **Physical Model** section.

The physics interface solves for $\mathbf{u}_l, p$, and

$$\tilde{\rho}_g = \rho_g \phi_g$$

the effective gas density. The gas velocity $\mathbf{u}_g$ is the sum of the following velocities:

$$\mathbf{u}_g = \mathbf{u}_l + \mathbf{u}_{slip} + \mathbf{u}_{drift} \qquad (6\text{-}98)$$

where $\mathbf{u}_{slip}$ is the relative velocity between the phases and $\mathbf{u}_{drift}$ is a drift velocity (see Turbulence Modeling in Bubbly Flow Applications). The physics interface calculates the gas density from the ideal gas law:

$$\rho_g = \frac{(p + p_{ref})M}{RT}$$

where M is the molecular weight of the gas (SI unit: kg/mol), R is the ideal gas constant (8.314472 J/(mol·K)), p_{ref} a reference pressure (SI unit: Pa), and T is temperature (SI unit: K). p_{ref} is a scalar variable, which by default is 1 atm (1 atmosphere or 101,325 Pa). The liquid volume fraction is calculated from

$$\phi_l = 1 - \phi_g$$

When there is a drift velocity, it has the form

$$\mathbf{u}_{drift} = -D_{gc}\frac{\nabla\phi_g}{\phi_g} \qquad (6\text{-}99)$$

where

$$D_{gc} = \frac{\mu_T}{\rho_l \sigma_T}$$

Here, μ_T is the turbulent viscosity, and σ_T is the turbulent Schmidt number.

Inserting Equation 6-99 and Equation 6-98 into Equation 6-95 gives

$$\frac{\partial \rho_g \phi_g}{\partial t} + \nabla \cdot (\phi_g \rho_g (\mathbf{u}_l + \mathbf{u}_{slip})) = \nabla \cdot (D_{gc}\, \rho_g \nabla \phi_g) - m_{gl}$$

That is, the drift velocity introduces a diffusive term in the gas transport equation. This is how the equation for the transport of the volume fraction of gas is actually implemented in the physics interface.

MASS TRANSFER AND INTERFACIAL AREA

It is possible to account for mass transfer between the two phases by specifying an expression for the mass transfer rate from the gas to the liquid m_{gl} (SI unit: kg/(m^3·s)).

The mass transfer rate typically depends on the interfacial area between the two phases. An example is when gas dissolves into a liquid. In order to determine the interfacial area, it is necessary to solve for the bubble number density (that is, the number of bubbles per volume) in addition to the phase volume fraction. The Bubbly Flow interface assumes that the gas bubbles can expand or shrink but not completely vanish, merge, or split. The conservation of the number density n (SI unit: $1/m^3$) then gives

$$\frac{\partial n}{\partial t} + \nabla \cdot (n(\mathbf{u}_l + \mathbf{u}_{slip})) = \nabla \cdot (D_{gc} \nabla n)$$

The number density and the volume fraction of gas give the interfacial area per unit volume (SI unit: m^2/m^3):

$$a = (4n\pi)^{1/3}(3\phi_g)^{2/3}$$

SLIP MODEL

The simplest possible approximation for the slip velocity $\mathbf{u}_{slip}$ is to assume that the bubbles always follow the liquid phase; that is, $\mathbf{u}_{slip} = \mathbf{0}$. This is known as homogeneous flow.

A better model can be obtained from the momentum equation for the gas phase. Comparing size of different terms, it can be argued that the equation can be reduced to a balance between the viscous drag force, $\mathbf{f}_D$ and the pressure gradient (Ref. 3), a so called pressure-drag balance:

$$\phi_l \nabla p = \mathbf{f}_D \tag{6-100}$$

Here $\mathbf{f}_D$ can be written as

$$\mathbf{f}_D = -C_d \frac{3}{4} \frac{\rho_l}{d_b} |\mathbf{u}_{slip}| \mathbf{u}_{slip} \tag{6-101}$$

where in turn d_b (SI unit: m) is the bubble diameter, and C_d (dimensionless) is the viscous drag coefficient. Given C_d and d_b, Equation 6-100 can be used to calculate the slip velocity. In practice, Equation 6-100 is multiplied by ϕ_l to reduce the slip velocity for large values of ϕ_g.

Schwarz and Turner (Ref. 4) proposed a linearized version of Equation 6-101 appropriate for air bubbles of 1–10 mm mean diameter in water:

$$\mathbf{f}_D = -C_W \mathbf{u}_{\text{slip}} \quad C_W = 5 \cdot 10^4 \ \frac{\text{kg}}{\text{m}^3 \cdot \text{s}} \tag{6-102}$$

The Hadamard–Rybczynski model is appropriate for small spherical bubbles with diameter less than 2 mm, and bubble Reynolds number less than one. The model uses the following expression for the drag coefficient (Ref. 5):

$$C_d = \frac{16}{\text{Re}_b}, \qquad \text{Re}_b = \frac{d_b \rho_1 |\mathbf{u}_{\text{slip}}|}{\mu_1}$$

For bubbles with diameter larger than 2 mm, the model suggested by Sokolichin, Eigenberger, and Lapin (Ref. 1) is a more appropriate choice:

$$C_d = \frac{0.622}{\dfrac{1}{\text{E\"o}} + 0.235}$$

where Eö is the Eötvös number

$$\text{E\"o} = \frac{g \rho_1 d_b^2}{\sigma}$$

Here, g is the magnitude of the gravity vector and σ the surface tension coefficient.

Turbulence Modeling in Bubbly Flow Applications

For most *bubbly flow* applications the flow field is turbulent. In that case, use a turbulence model and solve for the averaged velocity field. The Bubbly Flow, Turbulent Flow interfaces include the turbulence models described in Theory for the Turbulent Flow Interfaces, but the material properties of the liquid phase are used. In addition to the options of the single-phase flow model, in , , , , and it is also possible to account for bubble-induced turbulence — that is, extra production of turbulence due to relative motion between the gas bubbles and the liquid. The transport equation for the turbulent kinetic energy, k, includes a source term S_k which accounts for bubble-induced turbulence and is given by

$$S_k = -C_k \phi_g \nabla p \cdot \mathbf{u}_{\text{slip}}$$

The transport equation for the turbulent energy's dissipation rate, ε, includes the following source term:

$$C_\varepsilon S_\mathrm{k} \frac{\varepsilon}{k}$$

The following source term is added to the transport equation for the specific dissipation rate, ω:

$$\alpha_\omega S_\mathrm{k} \frac{\omega}{k}$$

Suitable values for the model parameters C_k, C_ε, and α_ω are not as well established as the parameters for single-phase flow. In the literature, values within the ranges $0.01 < C_\mathrm{k} < 1$, $1 < C_\varepsilon < 1.92$ have been suggested (Ref. 1), and α_ω can be defined as $\alpha_\omega = C_\varepsilon - 1$.

In the v2-f turbulence model, the ζ-equation also gets a contribution,

$$\left(2\frac{|\mathbf{u}_\mathrm{slip} \cdot \nabla l_\mathrm{w}|}{|\mathbf{u}_\mathrm{slip}| \cdot |\nabla l_\mathrm{w}|} - \zeta\right)\frac{S_\mathrm{k}}{k}$$

where l_w is the wall distance variable and its gradient gives the wall-normal direction. Such modeling assumes that the bubble-induced turbulence kinetic energy is pumped into the component of k aligned with $\mathbf{u}_\mathrm{slip}$.

The turbulent viscosity appears in the momentum equation and when adding a drift term to the gas velocity:

$$\mathbf{u}_\mathrm{drift} = -D_\mathrm{gc}\frac{\nabla\phi_\mathrm{g}}{\phi_\mathrm{g}}$$

Using a turbulence model that solves for the turbulent kinetic energy, k, together with a gas concentration that is not assumed to be low, the stress tensor contains an extra contribution, and the momentum equations becomes

$$\phi_1\rho_1\frac{\partial\mathbf{u}_1}{\partial t} + \phi_1\rho_1\mathbf{u}_1 \cdot \nabla\mathbf{u}_1 =$$

$$= -\nabla p + \nabla \cdot \left[\phi_1(\mu_1 + \mu_T)\left(\nabla\mathbf{u}_1 + \nabla\mathbf{u}_1^T - \frac{2}{3}(\nabla \cdot \mathbf{u}_1)\mathbf{I}\right) - \frac{2}{3}\phi_1\rho_1 k\mathbf{I}\right] + \phi_1\rho_1\mathbf{g} + \mathbf{F}$$

(6-103)

References for the Bubbly Flow Interfaces

1. A. Sokolichin, G. Eigenberger, and A. Lapin, "Simulations of Buoyancy Driven Bubbly Flow: Established Simplifications and Open Questions", *AIChE Journal*, vol. 50, no. 1, pp. 24–49, 2004.

2. D. Kuzmin and S. Turek, *Efficient Numerical Techniques for Flow Simulation in Bubble Column Reactors*, Institute of Applied Mathematics, University of Dortmund, 2000.

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4. M.P. Schwarz and W.J. Turner, "Applicability of the Standard k-ε Turbulence Model to Gas-stirred Baths", *Applied Mathematical Modelling*, vol. 12, pp. 273–279, 1988.

5. C. Crowe, M. Sommerfeld, and Y. Tsuji, *Multiphase Flows with Droplets and Particles*, CRC Press, 1998.

Theory for the Mixture Model Interface

The mixture model is a macroscopic two-phase flow model, in many ways similar to the bubbly flow model. It tracks the averaged phase concentration, or volume fraction, and solves a single momentum equation for the mixture velocity. It is suitable for mixtures consisting of solid particles or liquid droplets immersed in a liquid.

The Mixture Model interface theory is described in this section:

- The Mixture Model Equations
- Dispersed Phase Boundary Condition Equations
- Turbulence Modeling in Mixture Models
- Slip Velocity Models
- References for the Mixture Model Interfaces

The Mixture Model Equations

In the Mixture Model interfaces the particle-fluid combination is regarded as a single flowing continuum with macroscopic properties such as density and viscosity. The two phases consist of one dispersed phase and one continuous phase. The mixture model is valid if the continuous phase is a liquid, and the dispersed phase consists of solid particles, liquid droplets, or gas bubbles. For gas bubbles in a liquid, however, the bubbly flow model is preferable. The mixture model relies on the following assumptions:

- The density of each phase is approximately constant.
- Both phases share the same pressure field.
- The particle relaxation time is short compared to the time-scales of the macroscopic flow.

The mixture density is given by

$$\rho = \phi_c \rho_c + \phi_d \rho_d$$

where

- ϕ_c and ϕ_d denote the volume fractions of the continuous phase and the dispersed phase (SI unit: m^3/m^3), respectively
- ρ_c is the continuous phase density (SI unit: kg/m^3), and
- ρ_d is the dispersed phase density (SI unit: kg/m^3).

The volume flux for each phase is

$$\mathbf{j}_d = \phi_d \mathbf{u}_d$$

$$\mathbf{j}_c = \phi_c \mathbf{u}_c$$

where $\mathbf{u}_c$ and $\mathbf{u}_d$ (SI unit: m/s) are the continuous and the dispersed phase velocity vectors, respectively.

In previous versions of COMSOL Multiphysics (prior to version 5.4, see Mass-Averaged Mixture Velocity), the mixture velocity used was the mass-averaged mixture velocity $\mathbf{u}$ (SI unit: m/s), defined as

$$\mathbf{u} = \frac{\phi_c \rho_c \mathbf{u}_c + \phi_d \rho_d \mathbf{u}_d}{\rho} \tag{6-104}$$

The mixture velocity used here is the volume-averaged flux density, or volume-averaged mixture velocity $\mathbf{j}$ (SI unit: m/s), defined as

$$\mathbf{j} = \mathbf{j}_d + \mathbf{j}_c$$

The continuity equation for the mixture is

$$\rho_t + \nabla \cdot (\rho \mathbf{u}) = 0 \tag{6-105}$$

In the Mixture Model interfaces it is assumed that the densities of both phases, ρ_c and ρ_d, are constant, and therefore the following alternative form of the continuity equation for the mixture is used

$$\nabla \cdot \mathbf{j} = m_{dc}\left(\frac{1}{\rho_c} - \frac{1}{\rho_d}\right) \tag{6-106}$$

The momentum equation for the mixture is

$$\rho\mathbf{j}_t + \rho(\mathbf{j}\cdot\nabla)\mathbf{j} + \rho_c\varepsilon(\mathbf{j}_{\text{slip}}\cdot\nabla)\mathbf{j} = -\nabla p + \nabla\cdot\tau_{\text{Gm}} + \rho\mathbf{g} + \mathbf{F}$$
$$-\nabla\cdot[\rho_c(1+\phi_c\varepsilon)\mathbf{u}_{\text{slip}}\mathbf{j}_{\text{slip}}^T]$$
$$-\rho_c\varepsilon\left[(\mathbf{j}\cdot\nabla)\mathbf{j}_{\text{slip}} + (\nabla\cdot(D_{m\text{d}}\nabla\phi_\text{d}))\mathbf{j} + \mathbf{j}_{\text{slip}}m_{\text{dc}}\left(\frac{1}{\rho_c}-\frac{1}{\rho_\text{d}}\right)\right]$$

where:

- $\mathbf{j}$ is the velocity vector (SI unit: m/s)
- ρ is the density (SI unit: kg/m^3)
- p is the pressure (SI unit: Pa)
- ε is the reduced density difference (SI unit: kg/kg)
- $\mathbf{u}_{\text{slip}}$ is the slip velocity vector between the two phases (SI unit: m/s)
- $\mathbf{j}_{\text{slip}}$ is the slip flux (SI unit: m/s)
- τ_{Gm} is the sum of the viscous and turbulent stresses (SI unit: kg/(m·s^2))
- $D_{m\text{d}}$ is a turbulent dispersion coefficient (SI unit: m^2/s)
- m_{dc} is the mass transfer rate from the dispersed to the continuous phase (SI unit: kg/(m^3·s))
- $\mathbf{g}$ is the gravity vector (SI unit: m/s^2), and
- $\mathbf{F}$ is any additional volume force (SI unit: N/m^3)

The slip flux is defined for convenience as,

$$\mathbf{j}_{\text{slip}} = \phi_\text{d}\phi_c\mathbf{u}_{\text{slip}} \tag{6-107}$$

Here, $\mathbf{u}_{\text{slip}}$ (SI unit: m/s) denotes the relative velocity between the two phases. For different available models for the slip velocity, see Slip Velocity Models.

The reduced density difference ε is given by

$$\varepsilon = \frac{\rho_\text{d}-\rho_c}{\rho_c}$$

The sum of the viscous and turbulent stresses is

$$\tau_{\text{G}m} = (\mu+\mu_\text{T})[\nabla\mathbf{j}+\nabla\mathbf{j}^T]-\frac{2}{3}(\mu+\mu_\text{T})(\nabla\cdot\mathbf{j})\mathbf{I}-\frac{2}{3}\rho k\mathbf{I} \tag{6-108}$$

where μ (SI unit: Pa·s) is the mixture viscosity, μ_T (SI unit: Pa·s) the turbulent viscosity, and k (SI unit: m^2/s^2) is the turbulent kinetic energy, when available. If no turbulence model is used, μ_T and k equal zero

The transport equation for ϕ_d, the dispersed phase volume fraction, is

$$\frac{\partial}{\partial t}(\phi_d \rho_d) + \nabla \cdot (\phi_d \rho_d \mathbf{u}_d) = \nabla \cdot (\rho_d D_{md} \nabla \phi_d) - m_{dc} \qquad (6\text{-}109)$$

where m_{dc} (SI unit: kg/(m^3·s)) is the mass transfer rate from the dispersed to the continuous phase and D_{md} is a turbulent dispersion coefficient (SI unit: m^2/s) (see Turbulence Modeling in Mixture Models), accounting for extra diffusion due to turbulent eddies. When a turbulence model is not used, D_{md} is zero. Assuming constant density for the dispersed phase and using Equation 6-106, Equation 6-109 can be rewritten as

$$\frac{\partial}{\partial t}(\phi_d) + \mathbf{j} \cdot \nabla \phi_d + \nabla \cdot (\mathbf{j}_{slip}) = \nabla \cdot (D_{md} \nabla \phi_d) - \frac{m_{dc}\rho}{\rho_d \rho_c} \qquad (6\text{-}110)$$

The continuous phase volume fraction ϕ_c is

$$\phi_c = 1 - \phi_d$$

MASS TRANSFER AND INTERFACIAL AREA

It is possible to account for mass transfer between the two phases by specifying an expression for the mass transfer rate from the dispersed phase to the continuous m_{dc} (SI unit: kg/(m^3·s)).

The mass transfer rate typically depends on the interfacial area between the two phases. An example is when gas dissolves into a liquid. In order to determine the interfacial area, it is necessary to solve for the dispersed phase number density (that is, the number of particles per volume) in addition to the phase volume fraction. The Mixture Model interface assumes that the particles can increase or decrease in size but not completely vanish, merge, or split. The conservation of the number density n (SI unit: 1/m^3) then gives

$$\frac{\partial n}{\partial t} + \mathbf{j} \cdot \nabla n + \nabla \cdot (n\phi_c \mathbf{u}_{slip}) = \nabla \cdot (D_{md} \nabla n) - n m_{dc} \left(\frac{1}{\rho_c} - \frac{1}{\rho_d} \right)$$

The number density and the volume fraction dispersed particles give the interfacial area per unit volume (SI unit: m^2/m^3):

$$a = (4n\pi)^{1/3}(3\phi_d)^{2/3}$$

MASS-AVERAGED MIXTURE VELOCITY

In previous versions of COMSOL Multiphysics (prior to version 5.4), the mixture velocity used was the mass-averaged mixture velocity $\mathbf{u}$ (SI unit: m/s), see Equation 6-104. The continuity equation was

$$(\rho_c - \rho_d)\left[\nabla \cdot (\phi_d(1-c_d)\mathbf{u}_{slip} - D_{md}\nabla\phi_d) + \frac{m_{dc}}{\rho_d}\right] + \rho_c(\nabla \cdot \mathbf{u}) = 0 \qquad (6\text{-}111)$$

and the transport equation for ϕ_d was

$$\frac{\partial}{\partial t}(\phi_d) + \nabla \cdot (\phi_d\mathbf{u}_d) = \nabla \cdot (D_{md}\nabla\phi_d) - \frac{m_{dc}}{\rho_d} \qquad (6\text{-}112)$$

The dispersed phase velocity vector $\mathbf{u}_d$ and the mass fraction of the dispersed phase c_d are given by

$$\mathbf{u}_d = \mathbf{u} + (1-c_d)\mathbf{u}_{slip}$$

$$c_d = \frac{\phi_d\rho_d}{\rho}$$

The continuity equation Equation 6-111 is incompatible with the no-penetration condition of $\mathbf{u}$ at the walls, and $\mathbf{u}$ is not divergence-free. The volume-averaged velocity $\mathbf{j}$ is solenoidal and Equation 6-106 is compatible with the no-penetration condition at the walls (as long as there is no mass transfer or the densities of the two phases are equal).

Dispersed Phase Boundary Condition Equations

In addition to the boundary conditions for the mixture, specify boundary conditions for the dispersed phase on Wall, Inlet, and Outlet nodes. For these boundary types, the boundary condition's Settings window contains a Dispersed Phase Boundary Condition section.

DISPERSED PHASE CONCENTRATION

This is the default for the Inlet node. Specify the dispersed phase volume fraction:

$$\phi_d = \phi_{d0}$$

Enter the **Dispersed phase volume fraction** (dimensionless) in the ϕ_{d0} field.

If **Solve for interfacial area** is selected under the **Physical Model** section, the dispersed phase number density is also specified. The dispersed phase number density can be specified directly,

$$n = n_0$$

or, when **Diameter of particles/droplets** is selected, computed from the diameter of particles and droplets d_d:

$$n = 6\frac{\phi_{d0}}{\pi d_d^3}$$

DISPERSED PHASE OUTLET

This is the default for the Outlet node. This boundary condition is appropriate for boundaries where the dispersed phase leaves the domain with the dispersed phase velocity $\mathbf{u}_d$. No condition is imposed on the volume fractions at the boundary.

A corresponding flux condition is also applied for the number density equation (when **Solve for interfacial area** is selected under the **Physical Model** section).

DISPERSED PHASE FLUX

Using this boundary condition, specify the dispersed phase flux through the boundary:

$$-\mathbf{n} \cdot (\phi_d \mathbf{u}_d) = N_{\phi_d}$$

Enter the **Dispersed phase flux** (SI unit: m/s) in the N_{ϕ_d} field.

If **Solve for interfacial area** is selected under the **Physical Model** section, the number density flux through the boundary is also specified:

$$-\mathbf{n} \cdot (n \mathbf{u}_d) = N_{n_d}$$

SYMMETRY

This boundary condition, which is useful on boundaries that represent a symmetry line for the dispersed phase, sets the dispersed phase flux through the boundary to zero:

$$\mathbf{n} \cdot (\phi_d \mathbf{u}_d) = 0$$

A corresponding flux condition is also applied for the number density equation (when **Solve for interfacial area** is selected under the **Physical Model** section).

NO DISPERSED FLUX

This is the default for the Wall node. This boundary condition represents boundaries where the dispersed phase flux through the boundary is zero:

$$\mathbf{n} \cdot (\phi_d \mathbf{u}_d) = 0$$

In the case of moving and , the dispersed flux through the boundary is:

$$\mathbf{n} \cdot (\phi_d \mathbf{u}_d) = \mathbf{n} \cdot (\phi_d \mathbf{j})$$

This implies that the flux, relative to the boundary motion, is zero. A corresponding flux condition is also applied for the number density equation (when **Solve for interfacial area** is selected under the **Physical Model** section).

Turbulence Modeling in Mixture Models

Turbulence modeling is particularly relevant for dilute flows, that is, for flows with a low dispersed phase volume fraction. For dense flows, the mixture viscosity usually becomes high. In such cases, the flow is laminar and no turbulence modeling is necessary.

The Mixture Model, Turbulent Flow interfaces include the turbulence models described in Theory for the Turbulent Flow Interfaces.

The turbulence must be accounted for in the calculation of the dispersed phase volume fraction. This is accomplished by introducing a turbulent dispersion coefficient D_{md} (SI unit: m^2/s) in Equation 6-110 as

$$D_{md} = \frac{\mu_T}{\rho \sigma_T}$$

where σ_T is the turbulent particle Schmidt number (dimensionless). The particle Schmidt number is usually suggested as a value ranging from 0.35 to 0.7. In the physics interface the default value is 0.35. The so-called drift velocity is included in Equation 6-110 as a diffusion term

$$\frac{\partial}{\partial t}(\phi_d) + \mathbf{j} \cdot \nabla \phi_d + \nabla \cdot (\mathbf{j}_{\text{slip}}) = \nabla \cdot (D_{md} \nabla \phi_d) - \frac{m_{dc}\rho}{\rho_d \rho_c}$$

Similarly, the number density equation (used to compute the interfacial area) for turbulent flow corresponds to

$$\frac{\partial n}{\partial t} + \mathbf{j} \cdot \nabla n + \nabla \cdot (n\phi_c \mathbf{u}_{\text{slip}}) = \nabla \cdot (D_{md}\nabla n) - nm_{dc}\left(\frac{1}{\rho_c} - \frac{1}{\rho_d}\right)$$

The inclusion of the drift velocity in Equation 6-110 modifies the flux of the dispersed phase. The effective dispersed phase flux $\mathbf{j}_{d,\text{eff}}$ and velocity $\mathbf{u}_{d,\text{eff}}$ are given by

$$\mathbf{j}_{d,\text{eff}} = \mathbf{j}_d - D_{md}\nabla\phi_d$$

$$\mathbf{u}_{d,\text{eff}} = \mathbf{u}_d - \frac{D_{md}}{\phi_d}\nabla\phi_d$$

$\mathbf{j}_{d,\text{eff}}$ and $\mathbf{u}_{d,\text{eff}}$ are available in the physics interface as `mm.jdEff` and `mm.udEff`.

Slip Velocity Models

The Mixture Model interfaces contain three predefined models for the relative velocity between the two phases $\mathbf{u}_{\text{slip}}$ (SI unit: m/s):

- The *Schiller–Naumann model*
- The *Haider–Levenspiel model*
- The *Hadamard–Rybczynski model*

All three models use the following relation for the slip velocity:

$$\frac{3}{4}\frac{C_d}{d_d}|\mathbf{u}_{\text{slip}}|\mathbf{u}_{\text{slip}} = -\frac{(\rho - \rho_d)}{\rho_c}\left(-\mathbf{j}_t - (\mathbf{j} \cdot \nabla)\mathbf{j} + \mathbf{g} + \frac{\mathbf{F}}{\rho}\right) \qquad (6\text{-}113)$$

where C_d (dimensionless) is the particle drag coefficient. Essentially, interpret the relation as a balance between viscous drag and buoyancy forces acting on the dispersed phase.

The Schiller–Naumann model models the drag coefficient according to

$$C_d = \begin{cases} \dfrac{24}{\text{Re}_p}(1 + 0.15\text{Re}_p^{0.687}) & \text{Re}_p < 1000 \\ 0.44 & \text{Re}_p > 1000 \end{cases}$$

where Re_p is the particle Reynolds number

$$\text{Re}_p = \frac{d_d\rho_c|\mathbf{u}_{\text{slip}}|}{\mu}$$

Note that this definition of the particle Reynolds number uses the viscosity of the mixture and not the viscosity of the continuous phase, as would be customary for a single particle in a pure fluid with viscosity μ_c. This choice incorporates the hindrance effect of the other particles on the slip velocity, see Ref. 17.

Because the particle Reynolds number depends on the slip velocity, an implicit equation must be solved to obtain the slip velocity. Therefore, the Mixture Model interfaces add an additional equation for

$$|\mathbf{u}_{slip}|^2$$

when the Schiller–Naumann slip model is used. The Schiller–Naumann model is particularly well-suited for solid particles in a liquid.

The Haider–Levenspiel model is applicable to nonspherical particles. It models the drag coefficient according to

$$C_d = \frac{24}{Re_p}\left(1 + A(S_p)Re_p^{B(S_p)}\right) + \frac{C(S_p)}{1 + D(S_p)/Re_p}$$

where $A, B, C,$ and D are empirical correlations of the particle sphericity. The sphericity is defined as the ratio of the surface area of a volume equivalent sphere to the surface area of the considered nonspherical particle

$$0 < S_p = \frac{A_{sphere}}{A_{particle}} \le 1$$

The correlation coefficients are given by

$$A(S_p) = e^{2.3288 - 6.4581 S_p + 2.4486 S_p^2}$$
$$B(S_p) = 0.0964 + 0.5565 S_p$$
$$C(S_p) = e^{4.905 - 13.8944 S_p + 18.4222 S_p^2 - 10.2599 S_p^3}$$
$$D(S_p) = e^{1.4681 + 12.2584 S_p - 20.7322 S_p^2 + 15.8855 S_p^3}$$

The diameter used in the particle Reynolds number is that of the volume equivalent sphere. The equation for the squared slip velocity is also added when the Haider–Levenspiel slip model is used.

The Hadamard–Rybczynski drag law is valid for particle Reynolds numbers less than 1, for particles, bubbles, and droplets. The drag coefficient for liquid droplets or bubbles is

$$C_d = \frac{24}{\mathrm{Re}_p}\left(\frac{1 + \frac{2}{3}\frac{\mu_c}{\mu_d}}{1 + \frac{\mu_c}{\mu_d}}\right)$$

which yields the following explicit expression for the slip velocity

$$\mathbf{u}_{slip} = -\frac{(\rho - \rho_d)d_d^2}{18\mu}\left(\frac{1 + \frac{\mu_c}{\mu_d}}{1 + \frac{2}{3}\frac{\mu_c}{\mu_d}}\right)\left(-\mathbf{j}_t - (\mathbf{j} \cdot \nabla)\mathbf{j} + \mathbf{g} + \frac{\mathbf{F}}{\rho}\right)$$

For solid particles, the slip velocity is given by

$$\mathbf{u}_{slip} = -\frac{(\rho - \rho_d)d_d^2}{18\mu}\left(-\mathbf{j}_t - (\mathbf{j} \cdot \nabla)\mathbf{j} + \mathbf{g} + \frac{\mathbf{F}}{\rho}\right)$$

when $\mathrm{Re}_p < 1$. For very small gas bubbles, the drag coefficient is observed to be closer to the solid-particle value. This is believed to be caused by surface-active impurities collecting on the bubble surface.

References for the Mixture Model Interfaces

1. M. Manninen, V. Taivassalo, and S. Kallio, *On the Mixture Model for Multiphase Flow,* VTT Publications, 288, VTT Energy, Nuclear Energy, Technical Research Center of Finland (VTT), 1996.

2. C. Crowe, M. Sommerfeld, and Y. Tsuji, *Multiphase Flows with Droplets and Particles,* CRC Press, 1998.

3. M.S. Nigam, "Numerical Simulation of Buoyant Mixture Flows," *Int. Jour. of Multi. Flow.*, vol. 29, pp. 983–1015, 2003.

4. M. Ungarish, *Hydrodynamics of suspensions*, Springer-Verlag, 1993.

Theory for the Euler-Euler Interface

The Euler–Euler Model interfaces are based on averaging the Navier–Stokes equations for each present phase over a volume that is small compared to the computational domain but large compared to the dispersed phase (particles, droplets, or bubbles). The two phases, the continuous and the dispersed phase, are assumed to behave as two continuous and interpenetrating fluids, and the physics interface solves one set of momentum equations for each phase.

In this section:

- The Euler–Euler Model Equations
- Some Notes on Boundary Conditions
- Turbulent Two-Phase Flow Modeling
- References for the Euler–Euler Model Interfaces

The Euler–Euler Model Equations

MASS BALANCE

The following continuity relations hold for the continuous and dispersed phases (Ref. 3):

$$\frac{\partial}{\partial t}(\rho_c \phi_c) + \nabla \cdot (\rho_c \phi_c \mathbf{u}_c) = m_{dc} \tag{6-114}$$

$$\frac{\partial}{\partial t}(\rho_d \phi_d) + \nabla \cdot (\rho_d \phi_d \mathbf{u}_d) = -m_{dc} \tag{6-115}$$

Here ϕ (dimensionless) denotes the phase volume fraction, ρ (SI unit: kg/m^3) is the density, $\mathbf{u}$ (SI unit: m/s) the velocity of each phase, and m_{dc} is the mass transfer rate from the dispersed to the continuous phase (SI unit: kg/(m^3·s)). The subscripts c and d denote quantities relating to the continuous and the dispersed and phase, respectively. The following relation between the volume fractions must hold

$$\phi_c = 1 - \phi_d$$

Both phases are considered to be incompressible, in which case Equation 6-114 and Equation 6-115 can be simplified as:

$$\frac{\partial \phi_c}{\partial t} + \nabla \cdot (\phi_c \mathbf{u}_c) = \frac{m_{dc}}{\rho_c} \tag{6-116}$$

$$\frac{\partial \phi_d}{\partial t} + \nabla \cdot (\phi_d \mathbf{u}_d) = -\frac{m_{dc}}{\rho_d} \tag{6-117}$$

If Equation 6-117 and Equation 6-116 are added together, a continuity equation for the mixture is obtained:

$$\nabla \cdot (\phi_d \mathbf{u}_d + \mathbf{u}_c(1 - \phi_d)) = m_{dc}\left(\frac{1}{\rho_c} - \frac{1}{\rho_d}\right) \tag{6-118}$$

In order to control the mass balance of the two phases, the Euler–Euler Model interfaces solves Equation 6-117 together with Equation 6-118. Equation 6-117 is used to compute the volume fraction of the dispersed phase, and Equation 6-118 is used to compute the mixture pressure.

MOMENTUM BALANCE

The momentum equations for the continuous and dispersed phases, using the nonconservative forms (see for example Ref. 3 or Ref. 9), are:

$$\rho_c \phi_c \left[\frac{\partial}{\partial t}(\mathbf{u}_c) + \mathbf{u}_c \nabla \cdot (\mathbf{u}_c) \right] = \tag{6-119}$$
$$-\phi_c \nabla p + \phi_c \nabla \cdot \tau_c + \phi_c \rho_c \mathbf{g} + \mathbf{F}_{m,c} + \phi_c \mathbf{F}_c + m_{dc}(\mathbf{u}_{int} - \mathbf{u}_c)$$

$$\rho_d \phi_d \left[\frac{\partial}{\partial t}(\mathbf{u}_d) + \mathbf{u}_d \nabla \cdot (\mathbf{u}_d) \right] = \tag{6-120}$$
$$-\phi_d \nabla p + \phi_d \nabla \cdot \tau_d + \phi_d \rho_d \mathbf{g} + \mathbf{F}_{m,d} + \phi_d \mathbf{F}_d - m_{dc}(\mathbf{u}_{int} - \mathbf{u}_d)$$

Here p (SI unit: Pa) is the mixture pressure, which is assumed to be equal for the two phases. In the momentum equations the viscous stress tensor for each phase is denoted by τ (SI unit: Pa), $\mathbf{g}$ (SI unit: m/s^2) is the vector of gravitational acceleration, $\mathbf{F}_m$ (SI unit: N/m^3) is the interphase momentum transfer term (that is, the volume force exerted on each phase by the other phase), $\mathbf{F}$ (SI unit: N/m^3) is any other volume force term, and $\mathbf{u}_{int}$ is the interphase velocity (SI unit: m/s).

In these equations, the influence of surface tension in the case of liquid phases has been neglected, and the potential size distribution of the dispersed particles or droplets is not considered.

For fluid-solid mixtures where $\rho_d \gg \rho_c$, Equation 6-120 is modified in the manner of Enwald (Ref. 5)

$$
\rho_d \phi_d \left[\frac{\partial}{\partial t}(\mathbf{u}_d) + \mathbf{u}_d \nabla \cdot (\mathbf{u}_d) \right] =
$$
$$
- \phi_d \nabla p - \nabla p_s + \phi_d \rho_d \mathbf{g} + \mathbf{F}_{m,d} + \phi_d \mathbf{F}_d - m_{dc}(\mathbf{u}_{int} - \mathbf{u}_d)
$$
(6-121)

where p_s (SI unit: Pa) is the solid pressure.

The fluid phases in the above equations are assumed to be Newtonian and the viscous stress tensors are defined as

$$
\tau_c = \mu_c^m \left(\nabla \mathbf{u}_c + (\nabla \mathbf{u}_c)^T - \frac{2}{3}(\nabla \cdot \mathbf{u}_c)\mathbf{I} \right)
$$

$$
\tau_d = \mu_d^m \left(\nabla \mathbf{u}_d + (\nabla \mathbf{u}_d)^T - \frac{2}{3}(\nabla \cdot \mathbf{u}_d)\mathbf{I} \right)
$$

where μ_c^m and μ_d^m (SI unit: Pa·s) are the dynamic viscosity model of the respective phase. Observe how the viscous terms in equation Equation 6-119 and Equation 6-120 appear with their volume fractions outside the divergence operators. The equations can also be derived so that the terms read $\nabla \cdot (\phi_c \tau_c)$ and $\nabla \cdot (\phi_d \tau_d)$ instead (see for example Ref. 4 or Ref. 5). It depends on exactly how the derivation is carried out. formulation in Equation 6-119 and Equation 6-120 are so that the momentum equation can be divided by ϕ_c and ϕ_d respectively as described below.

In order to avoid singular solutions when the volume fractions tend to zero, the governing equations above are divided by the corresponding volume fraction. The implemented momentum equation for the continuous phase is:

$$
\rho_c \frac{\partial}{\partial t}(\mathbf{u}_c) + \rho_c \mathbf{u}_c \nabla \cdot (\mathbf{u}_c) = - \nabla p + \nabla \cdot \tau_c + \rho_c \mathbf{g} + \frac{\mathbf{F}_{m,c}}{\phi_c} + \mathbf{F}_c + \frac{m_{dc}}{\phi_c}(\mathbf{u}_{int} - \mathbf{u}_c)
$$

The implemented momentum equations for the dispersed phase in the case of dispersed liquid droplets or bubbles is:

$$
\rho_d \left[\frac{\partial}{\partial t}(\mathbf{u}_d) + \mathbf{u}_d \nabla \cdot (\mathbf{u}_d) \right] =
$$
$$
- \nabla p + \nabla \cdot \tau_d + \rho_d \mathbf{g} + \frac{\mathbf{F}_{m,d}}{\phi_d} + \mathbf{F}_d - \frac{m_{dc}}{\phi_d}(\mathbf{u}_{int} - \mathbf{u}_d)
$$
(6-122)

and in the case of dispersed solid particles:

$$\rho_d \left[\frac{\partial}{\partial t}(\mathbf{u}_d) + \mathbf{u}_d \nabla \cdot (\mathbf{u}_d) \right] =$$
$$-\nabla p - \frac{\nabla p_s}{\phi_d} + \rho_d \mathbf{g} + \frac{\mathbf{F}_{m,d}}{\phi_d} + \mathbf{F}_d - \frac{m_{dc}}{\phi_d}(\mathbf{u}_{int} - \mathbf{u}_d) \tag{6-123}$$

VISCOSITY MODELS

The Newtonian viscosities of interpenetrating media are not readily available. Instead empirical and analytical models for the dynamic viscosity of the two-phase mixture have been developed by various researchers, usually as a function of the dispersed volume fraction. Using an expression for the mixture viscosity, the default values for the dynamic viscosities of the two interpenetrating phases are taken to be:

$$\mu_c^m = \mu_d^m = \mu_{mix} \tag{6-124}$$

A simple mixture viscosity covering the entire range of particle concentrations is the Krieger type model (Ref. 5):

$$\mu_{mix} = \mu_c \left(1 - \frac{\phi_d}{\phi_{d,max}} \right)^{-2.5\phi_{d,max}} \tag{6-125}$$

Here $\phi_{d,max}$ is the maximum packing limit, by default 0.62 for solid particles. Equation 6-125 can be applied when $\mu_c \ll \mu_d$. An extension of Equation 6-125 can be applied for liquid droplets/bubbles:

$$\mu_{mix} = \mu_c \left(1 - \frac{\phi_d}{\phi_{d,max}} \right)^{-2.5\phi_{d,max}\frac{\mu_d + 0.4\mu_c}{\mu_d + \mu_c}} \tag{6-126}$$

For liquid droplets/bubbles the default value of $\phi_{d,max}$ is 1.

For fluid-fluid systems, the simple relation

$$\mu_{mix} = \phi_c \mu_c + \phi_d \mu_d \tag{6-127}$$

can sometimes be applied or the viscosity for each individual phase can be applied to the respective momentum equation.

An alternative to mixture viscosity for dispersed solid particles, that is particles in gas flow, is to model the particle interface with a solid pressure instead (see Solid Pressure).

A small viscosity is however necessary for numerical robustness and Gidaspow (Ref. 6) suggested to use

$$\mu_d^m = 0.5 \max(\phi_d, \phi_{d,res}) \tag{6-128}$$

This is consistent with the requirement that $\mu_d^m \to 0$ when $\phi_d \to 0$ (Ref. 9), but in practice it can suffice with any small enough, nonzero value.

INTERPHASE MOMENTUM TRANSFER

In all the equations, $\mathbf{F}_m$ denotes the interphase momentum transfer, that is the force imposed on one phase by the other phase. Considering a particle, droplet, or bubble in a fluid flow, it is affected by a number of forces, for example, the drag force, the added mass force, the Basset force, and the lift force. The most important force is usually the drag force, especially in fluids with a high concentration of dispersed solids, and hence this is the predefined force included in the Euler–Euler model. The drag force added to the momentum equation is defined as:

$$\mathbf{F}_{drag,c} = -\dot{\mathbf{F}}_{drag,d} = \beta \mathbf{u}_{slip} \tag{6-129}$$

where β is a drag force coefficient and the slip velocity is defined as

$$\mathbf{u}_{slip} = \mathbf{u}_d - \mathbf{u}_c$$

	The drag force on the dispersed phase is equal to the one on the continuous phase but is working in the opposite direction.

The drag force coefficient, β, is for solid particles often written as (Ref. 2)

$$\beta = \frac{3}{4d_d} \phi_d C_D \rho_c |\mathbf{u}_{slip}| \tag{6-130}$$

For fluid-fluid system, Equation 6-130 is regularized to read (Ref. 12)

$$\beta = \frac{3}{4d_d} \phi_d \phi_c C_D \rho_c |\mathbf{u}_{slip}| \tag{6-131}$$

which is consistent with a vanishing β if $\phi_c \to 0$. All drag force models except Gidaspow are based on Equation 6-130 for solid particles and on Equation 6-131 for bubbles and droplets.

Gidaspow

For dense particle flows with a high concentration of the dispersed phase — for example, in fluidized bed models — the Gidaspow model (Ref. 6) for the drag coefficient can be used. It combines the Wen and Yu (Ref. 7) fluidized state expression:

For $\phi_c > 0.8$

$$\beta = \frac{3\phi_c\phi_d\rho_c C_d}{4d_d}|\mathbf{u}_{slip}|\phi_c^{-2.65} \tag{6-132}$$

with the Ergun (Ref. 8) packed bed expression:

For $\phi_c < 0.8$

$$\beta = 150\frac{\mu_c\phi_d^2}{\phi_c d_d^2} + 1.75\frac{\phi_d\rho_c}{d_d}|\mathbf{u}_{slip}| \tag{6-133}$$

In the above equations, d_d (SI unit: m) is the dispersed particle diameter, and C_d is the drag coefficient for a single dispersed particle. The drag coefficient is in general a function of the particle Reynolds number

$$\mathrm{Re}_p = \frac{d_d\rho_c|\mathbf{u}_{slip}|}{\mu_c}$$

No universally valid expression for the drag coefficient exists. Using the implemented Gidaspow model, C_d is computed using the Schiller–Naumann relation.

Schiller–Naumann

The Schiller–Naumann model describes the drag coefficient in Equation 6-130 and Equation 6-131 for a single rigid sphere (see for example Ref. 3)

$$C_d = \begin{cases} \dfrac{24}{\mathrm{Re}_p}(1 + 0.15\mathrm{Re}_p^{0.687}) & \mathrm{Re}_p < 1000 \\ 0.44 & \mathrm{Re}_p > 1000 \end{cases} \tag{6-134}$$

It is valid for particle Reynolds numbers up to some critical Reynolds number, approximately equal to $2.5 \cdot 10^5$ where drag crisis occurs.

The Schiller–Naumann model is appropriate for diluted flows since the correlation in Equation 6-134 is based on a single particle and does not take particle-particle interaction into account.

The Schiller–Naumann model can be applied to small fluid particles since they do not deform significantly.

Hadamard–Rybczynski

The Hadamard–Rybczynski drag law is valid for dilute flows with particle Reynolds number less than one for particles, bubbles, and droplets and is defined as:

$$C_d = \frac{24}{\mathrm{Re_p}} \left(\frac{1 + \frac{2}{3}\frac{\mu_c}{\mu_d}}{1 + \frac{\mu_c}{\mu_d}} \right)$$

for bubbles and droplets and as

$$C_d = \frac{24}{\mathrm{Re_p}}$$

for solid particles (the Stokes limit). For very small gas bubbles, the drag coefficient is observed to be closer to the solid-particle value. This is believed to be caused by surface-active impurities collecting on the bubble surface.

Ishii–Zuber

The Ishii–Zuber model (Ref. 10) can for solid particles be regarded as a generalization of the Schiller–Naumann model. For solid particles it can be formulated as

$$C_D = \max\left(\frac{24}{\mathrm{Re_m}}[1 + 0.1\mathrm{Re_m^{0.75}}], 0.45 \left[\frac{1 + 17.67 f(\phi_d)^{6/7}}{18.67 f(\phi_d)} \right] \right) \tag{6-135}$$

where

$$f(\phi_d) = \sqrt{\phi_c}(\mu_c/\mu_m) \tag{6-136}$$

and $\mathrm{Re_m}$ is a Reynolds number based on the mixture viscosity

$$\mathrm{Re_m} = \frac{d_d \rho_c |\mathbf{u}_{slip}|}{\mu_m} \tag{6-137}$$

The Ishii–Zuber model is formulated with the assumption that μ_m is described by a Krieger type model (Equation 6-125 for solids or Equation 6-126 for droplets and bubbles). The dependence on μ_m means that the Ishii–Zuber model is valid also for dense suspensions.

For bubbles and droplets, Ishii and Zuber identify three regimes. At low Reynolds numbers, bubbles and droplets behave in the same way as solid particles and the drag coefficient can be described by

$$C_{D,\,visc} = \frac{24}{Re_m}[1 + 0.1 Re_m^{0.75}] \tag{6-138}$$

When the Reynolds number becomes higher, bubbles and droplets start to deform in such a way that the drag coefficient increases linearly with diameter but is independent of viscosity. Ishii and Zuber refer to this as the distorted particle regime and suggest the following correlation for this regime:

$$C_{D,\,dist} = \frac{2}{3}\sqrt{Eo}\left[\frac{1 + 17.67 f(\phi_d)^{6/7}}{18.67 f(\phi_d)}\right] \tag{6-139}$$

where Eo is the Eötvös number

$$Eo = \frac{g|\rho_c - \rho_d|d_d^2}{\sigma} \tag{6-140}$$

where in turn g is the gravitational constant and σ is the surface tension coefficient. The Eötvös number relates surface tension forces to gravitational forces. The second, "distorted" regime ends when hydrodynamic instabilities prevents the drag from increasing further and the distorted regime is capped by the following value:

$$C_{D,\,cap} = \frac{8}{3}\phi_c^2 \tag{6-141}$$

The complete model for bubbles and droplets can hence be written:

$$C_D = \begin{cases} C_{D,\,visc} & \text{if } C_{D,\,visc} \geq C_{D,\,dist} \\ \min(C_{D,\,dist}, C_{D,\,cap}) & \text{if } C_{D,\,visc} < C_{D,\,dist} \end{cases} \tag{6-142}$$

Haider–Levenspiel
The Haider–Levenspiel model is applicable to dilute flows with nonspherical solid particles. It models the drag coefficient according to

$$C_d = \frac{24}{Re_p}\left(1 + A(S_p)Re_p^{B(S_p)}\right) + \frac{C(S_p)}{1 + D(S_p)/Re_p}$$

where A, B, C, and D are empirical correlations of the particle sphericity (see for further details).

Tomiyama and Others

Tomiyama and others (Ref. 11) provided three correlations for diluted bubbles and droplets. The correlation for purified fluids read

$$C_D = \max\left\{\min\left[\frac{16}{\mathrm{Re}_p}(1+0.15\mathrm{Re}_p^{0.687}), \frac{48}{\mathrm{Re}_p}\right], \frac{8}{3}\frac{\mathrm{Eo}}{\mathrm{Eo}+4}\right\} \tag{6-143}$$

Fluid pure enough for Equation 6-143 to be valid is typically only achievable in laboratory environments. Even small amounts of surface-active impurities can collect at the droplet/bubble interface and cause a surface tension gradient which resists surface movement. The correlation for slightly contaminated fluids therefore prescribe a slightly higher drag coefficient:

$$C_D = \max\left\{\min\left[\frac{24}{\mathrm{Re}_p}(1+0.15\mathrm{Re}_p^{0.687}), \frac{72}{\mathrm{Re}_p}\right], \frac{8}{3}\frac{\mathrm{Eo}}{\mathrm{Eo}+4}\right\} \tag{6-144}$$

This correlation is the default one and applies to droplets and bubbles in fluids of contamination levels comparable to ordinary tap water.

When the contamination level is high, the impurities effectively prevent all motion within the droplet or bubble and the following correlation is suggested:

$$C_D = \max\left\{\min\frac{24}{\mathrm{Re}_p}(1+0.15\mathrm{Re}_p^{0.687}), \frac{8}{3}\frac{\mathrm{Eo}}{\mathrm{Eo}+4}\right\} \tag{6-145}$$

SOLID PRESSURE

For fluid-solid mixtures where $\rho_d \gg \rho_c$, for example solid particles in gas flow, a model for the solid pressure, p_s in Equation 6-123, is needed. The solid pressure models the particle interaction due to collisions and friction between the particles. The solid pressure model implemented uses a gradient diffusion based assumption:

$$\nabla p_s = -G(\phi_c)\nabla\phi_c$$

where the empirical function G can be thought of as a modulus of elasticity or powder modulus. A common form for G is (Ref. 5)

$$G(\phi_c) = 10^{B_1\phi_c + B_2} \tag{6-146}$$

The available predefined models (all defined in Ref. 5) are those of Gidaspow and Ettehadieh,

$$G(\phi_c) = 10^{-8.76\phi_c + 5.43} \qquad (6\text{-}147)$$

Ettehadieh,

$$G(\phi_c) = 10^{-10.46\phi_c + 6.577} \qquad (6\text{-}148)$$

and Gidaspow,

$$G(\phi_c) = 10^{-10.5\phi_c + 9.0} \qquad (6\text{-}149)$$

Observe that the solid pressure term theoretically replaces the stress term in the dispersed phase momentum equation. A small viscosity is however necessary for numerical robustness. The Gidaspow formulation or a small constant value is appropriate. The viscosity for the continuous phase, μ_c^m, can be taken as the single phase value, that is $\mu_c^m = \mu_c$.

NOTES ON THE IMPLEMENTATION

There are several equations with potentially singular terms and expressions such as the term

$$\frac{\mathbf{F}_{m,d}}{\phi_d}$$

in Equation 6-122. Also, ϕ_d is a degree of freedom and can therefore, during computations, obtain unphysical values in small areas. This can, in turn, lead to unphysical values of material properties such as viscosity and density. To avoid these problems, the implementation uses the following regularizations:

- $1/\phi_k$, $k = c,d$ is replaced by $1/\phi_{k,pos}$ where

$$\phi_{k,pos} = \max(\phi_k, \phi_{k,res})$$

  The residue volume fractions are per default set to 10^{-4} but can be changed in the section of the interface settings.

- When appropriate, for example when evaluating drag models and mixture viscosities, ϕ_k, $k = c,d$ are replaced by

$$\phi_{k,\,reg} = \min(\max(\phi_k, 0), 1)$$

Note however that the continuity equation, Equation 6-118, uses ϕ_k without regularization in order to guarantee mass conservation.

Some Notes on Boundary Conditions

An effect of dividing the momentum equations with ϕ_c and ϕ_d, respectively is that for example $\mathbf{u}_d$ obtains a value even if $\phi_d = 0$. In many cases $\mathbf{u}_d$ will tend to $\mathbf{u}_c$ in lack of a dispersed phase. So on inlets where $\phi_d = 0$, it is appropriate to set $\mathbf{u}_d = \mathbf{u}_c$.

A fixed value for ϕ_d should only be prescribed if there is no transport of ϕ_d toward the inlet. If, for example, a cloud of dispersed phase with higher ϕ_d than the prescribed value somehow reaches the inlet, ϕ_d will actually be "consumed".

When specifying a dispersed phase flux, make sure to specify an appropriate velocity to go with the flux to avoid unphysical concentrations of ϕ_d close to the boundary.

At walls, where it is possible to prescribe a wall leakage, the continuous phase normal velocity is set to

$$\mathbf{u}_c \cdot \mathbf{n} = -\frac{\dot{m}_c}{\rho_c \phi_{c,\,pos}}$$

For a dispersed phase leakage:

$$\mathbf{u}_d \cdot \mathbf{n} = -\frac{\dot{m}_d}{\rho_d \phi_{d,\,pos}}$$

Wall leakage for one phase works best if combined with slip condition for the other phase so that the mixture is given maximum freedom to react to the leakage.

Turbulent Two-Phase Flow Modeling

When the characteristic Reynolds number of the two-phase mixture under investigation becomes high, the flow transitions and becomes turbulent. The influence of the turbulence on the flow characteristics (mixing, particle dispersion, pressure drop, and so on) are usually significant and warrants the use of a turbulence model.

In order to model fluid flow turbulence, the Euler–Euler Model, Turbulent Flow interface uses the k-ε turbulence model. This is realized by solving transport equations

for the kinetic energy k (SI unit: m^2/s^2) and the dissipation rate of turbulent kinetic energy ε (SI unit: m^2/s^3).

The interface includes the possibility to model the turbulent flow of the two-phase mixture, or to solve for turbulent flow of each phase separately. In the former case, one set of k-ε equations are solved, while in the latter two sets of k-ε equations are solved for, one for each phase.

MIXTURE TURBULENCE

Mixture turbulence assumes that the turbulence effects on both the continuous and dispersed phase can be modeled by solving for the turbulence of the resulting two-phase mixture. Here this is done using a two-equation k-ε model where the transport of turbulence quantities is based on the mass-averaged mixture velocity

$$\mathbf{u}_m = \frac{\phi_c \rho_c \mathbf{u}_m + \phi_d \rho_d \mathbf{u}_m}{\rho},$$

and a volume-averaged mixture viscosity

$$\mu_m = \phi_c \mu_c^m + \phi_d \mu_d^m$$

This implies that the model is appropriate for flows where the relaxation time of the dispersed particles (the time scale on which particles react to changes in the carrier fluid velocity) is not significantly different to the time scale of the turbulence. It is also appropriate for stratified flows, where the mixture mainly consists of one of the phases.

Setting the **Two-phase turbulence** interface property to **Mixture**, the turbulence of the two-phase flow is modeled by solving the following k and ε equations:

$$\rho \frac{\partial k}{\partial t} + \rho \mathbf{u}_m \cdot \nabla k = \nabla \cdot \left(\left(\mu_m + \frac{\mu_T}{\sigma_k} \right) \nabla k \right) + P_k - \rho \varepsilon \tag{6-150}$$

$$\rho \frac{\partial \varepsilon}{\partial t} + \rho \mathbf{u}_m \cdot \nabla \varepsilon = \nabla \cdot \left(\left(\mu_m + \frac{\mu_T}{\sigma_\varepsilon} \right) \nabla \varepsilon \right) + C_{\varepsilon 1} \frac{\varepsilon}{k} P_k - C_{\varepsilon 2} \rho \frac{\varepsilon^2}{k} \tag{6-151}$$

The equations correspond to the standard two-equation k-ε model including realizability constraints.

The production term is defined accordingly as

$$P_k = \mu_\text{T}\left(\nabla\mathbf{u}_\text{m}{:}(\nabla\mathbf{u}_\text{m} + (\nabla\mathbf{u}_\text{m})^T) - \frac{2}{3}(\nabla\cdot\mathbf{u}_\text{m})^2\right) - \frac{2}{3}\rho k\nabla\cdot\mathbf{u}_\text{m}$$

and the resulting turbulent viscosity is defined as

$$\mu_T = \rho C_\mu\frac{k^2}{\varepsilon}$$

where C_μ is a model constant. The viscous stress tensors for the phases are hence defined as

$$\tau_\text{c} = (\mu_\text{c}^\text{m} + \mu_T)\left(\nabla\mathbf{u}_\text{c} + (\nabla\mathbf{u}_\text{c})^T - \frac{2}{3}(\nabla\cdot\mathbf{u}_\text{c})\mathbf{I}\right) - \frac{2}{3}\rho_\text{c} k\mathbf{I},$$

$$\tau_\text{d} = (\mu_\text{d}^\text{m} + \mu_T)\left(\nabla\mathbf{u}_\text{d} + (\nabla\mathbf{u}_\text{d})^T - \frac{2}{3}(\nabla\cdot\mathbf{u}_\text{d})\mathbf{I}\right) - \frac{2}{3}\rho_\text{d} k\mathbf{I}.$$

Assuming mixture turbulence, the transport equation for the volume fraction is:

$$\frac{\partial}{\partial t}(\phi_\text{d}) + \nabla\cdot(\phi_\text{d}\mathbf{u}_d) = \nabla\cdot(D_{m\text{d}}\nabla\phi_\text{d}) \tag{6-152}$$

Here the dispersion of the particulate phase by the turbulent fluctuations is modeled using a gradient based hypothesis. The turbulent dispersion coefficient is defined from the turbulent viscosity of the two-phase mixture in the manner of

$$D_{m\text{d}} = \frac{\mu_T}{\rho\sigma_T}$$

where σ_T is a turbulent particle Schmidt number (dimensionless).

The default values of the dimensionless parameters using the Mixture Two-phase turbulence model are:

CONSTANT	VALUE
C_μ	0.09
$C_{\varepsilon 1}$	1.44
$C_{\varepsilon 2}$	1.92
σ_k	1.0
σ_ε	1.3
K_v	0.41

CONSTANT	VALUE
B	5.2
σ_T	0.35

PHASE-SPECIFIC TURBULENCE

The phase-specific Two-phase turbulence model assumes that the turbulent flow of the continuous and dispersed phase can be modeled by solving for the turbulence of each phase separately by using two sets of k-ε equations. The model implies that the time scales of the turbulent flow of each phase can differ, but it is also computationally more expensive than assuming solving one set of k-ε equations for the mixture.

Setting the **Two-phase turbulence** interface property to **Phase specific**, the turbulent flow of the two phases is modeled by solving two sets of k and ε equations, one for each phase. For the continuous phase, the transport equations for k and ε are

$$\rho_c \frac{\partial k_c}{\partial t} + \rho_c \mathbf{u}_c \cdot \nabla k_c = \nabla \cdot \left(\left(\mu_c^m + \frac{\mu_{T,c}}{\sigma_{k,c}} \right) \nabla k_c \right) + P_{k,c} - \rho_c \varepsilon_c \qquad (6\text{-}153)$$

$$\rho_c \frac{\partial \varepsilon_c}{\partial t} + \rho_c \mathbf{u}_c \cdot \nabla \varepsilon_c = \nabla \cdot \left(\left(\mu_c^m + \frac{\mu_{T,c}}{\sigma_{\varepsilon,c}} \right) \nabla \varepsilon_c \right) + C_{\varepsilon1,c} \frac{\varepsilon_c}{k_c} P_{k,c} - C_{\varepsilon2,c} \rho \frac{\varepsilon_d^2}{k_d} \qquad (6\text{-}154)$$

while for the dispersed phase the corresponding equations are

$$\rho_d \frac{\partial k_d}{\partial t} + \rho_d \mathbf{u}_d \cdot \nabla k_d = \nabla \cdot \left(\left(\mu_d^m + \frac{\mu_{T,d}}{\sigma_{k,d}} \right) \nabla k_d \right) + P_{k,d} - \rho_d \varepsilon_d \qquad (6\text{-}155)$$

$$\rho_d \frac{\partial \varepsilon_d}{\partial t} + \rho_d \mathbf{u}_d \cdot \nabla \varepsilon_d = \nabla \cdot \left(\left(\mu_d^m + \frac{\mu_{T,d}}{\sigma_{\varepsilon,d}} \right) \nabla \varepsilon_d \right) + C_{\varepsilon1,d} \frac{\varepsilon_d}{k_d} P_{k,d} - C_{\varepsilon2,d} \rho \frac{\varepsilon_d^2}{k_d} \qquad (6\text{-}156)$$

The equations for each phase correspond to the standard two-equation k-ε model including realizability constraints.

The production terms are defined as

$$P_{k,c} = \mu_{T,c} \left(\nabla \mathbf{u}_c : (\nabla \mathbf{u}_c + (\nabla \mathbf{u}_c)^T) - \frac{2}{3} (\nabla \cdot \mathbf{u}_c)^2 \right) - \frac{2}{3} \rho_c k_d \nabla \cdot \mathbf{u}_c$$

$$P_{k,d} = \mu_{T,d} \left(\nabla \mathbf{u}_d : (\nabla \mathbf{u}_d + (\nabla \mathbf{u}_d)^T) - \frac{2}{3} (\nabla \cdot \mathbf{u}_d)^2 \right) - \frac{2}{3} \rho_d k_d \nabla \cdot \mathbf{u}_d$$

The resulting turbulent viscosity, applied individually in the momentum equations of the continuous and the dispersed phases, are

$$\mu_{T,c} = \rho_c C_{\mu,c} \frac{k_c^2}{\varepsilon_c}, \ \mu_{T,d} = \rho_d C_{\mu,d} \frac{k_d^2}{\varepsilon_d} \tag{6-157}$$

where $C_{\mu,c}$ and $C_{\mu,d}$ are model constants. The viscous stress tensors for the phases are hence defined as

$$\tau_c = (\mu_c^m + \mu_{T,c})\left(\nabla \mathbf{u}_c + (\nabla \mathbf{u}_c)^T - \frac{2}{3}(\nabla \cdot \mathbf{u}_c)\mathbf{I}\right) - \frac{2}{3}\rho_c k_c \mathbf{I},$$

$$\tau_d = (\mu_d^m + \mu_{T,d})\left(\nabla \mathbf{u}_d + (\nabla \mathbf{u}_d)^T - \frac{2}{3}(\nabla \cdot \mathbf{u}_d)\mathbf{I}\right) - \frac{2}{3}\rho_d k_d \mathbf{I}.$$

As in the case of mixture turbulence, the dispersion of the particulate phase by the turbulent fluctuations is modeled using a gradient based hypothesis (Equation 6-152). For phase-specific turbulence the dispersion coefficient is modeled as a volume average of the respective turbulent diffusivity of each phase

$$D_{md} = \frac{1}{\sigma_{T,d}}\left(\phi_c \frac{\mu_{T,c}}{\rho_c} + \phi_d \frac{\mu_{T,d}}{\rho_d}\right)$$

using a turbulent particle Schmidt number $\sigma_{T,d}$ (dimensionless).

The default values of the turbulence model parameters for phase specific turbulence are

CONTINUOUS PHASE CONSTANTS	VALUE	DISPERSED PHASE CONSTANTS	VALUE
$C_{\mu,c}$	0.09	$C_{\mu,d}$	0.09
$C_{\varepsilon1,c}$	1.44	$C_{\varepsilon1,d}$	1.44
$C_{\varepsilon2,c}$	1.92	$C_{\varepsilon2,d}$	1.92
$\sigma_{k,c}$	1.0	$\sigma_{k,d}$	1.0
$\sigma_{\varepsilon,c}$	1.3	$\sigma_{\varepsilon,d}$	1.3
$K_{v,c}$	0.41	$K_{v,d}$	0.41
B_c	5.2	B_d	5.2
		$\sigma_{T,d}$	0.35

References for the Euler–Euler Model Interfaces

1. M.J.V. Goldschmidt, B.P.B. Hoomans, and J.A.M. Kuipers, "Recent Progress Towards Hydrodynamic Modelling of Dense Gas-Particle Flows", *Recent Research Developments in Chemical Engineering*, Transworld Research Network, India, pp. 273–292, 2000.

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Theory for the Coupling of Fluid Flow to Electrochemical Reactions

Also see Theory for the Coupling of Mass Transport to Electrochemical Reactions for how to calculate molar and mass fluxes, sources, and sinks.

Momentum Sources and Sinks

The flow velocity, $\mathbf{u}$ (SI unit: m/s), at a boundary is coupled to the total mass flux of the species at the electrode surface in the following way

$$\mathbf{u} \cdot \mathbf{n} = \frac{1}{\rho} \sum_i \mathbf{n}_i \cdot \mathbf{n} \tag{6-158}$$

where ρ (SI unit: kg/m^3) is the density of the flowing media, $\mathbf{n}$ the surface normal and $\mathbf{n}_i$ is the mass flux of species i.

For flow interfaces solving for the velocity field, no-slip conditions are applied at the electrode surface, resulting in

$$\mathbf{u} = -\left(\frac{1}{\rho} \sum_i M_i N_i\right)\mathbf{n} \tag{6-159}$$

where M_i (SI unit: kg/mol) is the species mass and N_i (SI unit: mol/(m^2·s)) the molar flux calculated by Faraday's law.

For a porous electrode the sum of all mass fluxes are added to the conservation equation according to:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = \sum_i R_{i,\,\text{mass}} \tag{6-160}$$

Note that because the mass is usually not conserved within the species transporting phase (the right-hand side above being nonzero), the velocity field is not divergence free.

7

Heat Transfer Interfaces

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 relevant for systems based on chemical reactions and mass transfer along with fluid flow. These physics interfaces are found under the **Heat Transfer** branch (⌇).

The basic functionality for simulating heat transfer in homogeneous media is described in The Heat Transfer Interfaces in the *COMSOL Multiphysics Reference Manual*. The Fuel Cell & Electrolyzer Module has extra functionality for simulating heat transfer in porous media. The documentation of The Heat Transfer in Porous Media Interface is found in the *Heat Transfer Module User's Guide*, which is supplied with the Fuel Cell & Electrolyzer Module irrespective of whether a separate Heat Transfer Module license is purchased.

Most electrochemistry interfaces automatically define heat source variables that may be coupled to the heat transfer interfaces either manually or by the use of a Electrochemical Heating multiphysics node. See the Theory for Electrochemical Heat Sources section in the Electrochemistry Interfaces chapter for more information on how these heat source variables are computed.

8

Thermodynamics

This chapter describes how you can use the thermodynamics functionality to define thermo-physical and transport properties. These properties 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

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, for example, 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, that is, 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** (⬜). When the model includes a Component, **Thermodynamics** is also available in the **Physics** toolbar.

Using the Reaction Engineering or Chemistry interfaces, **Thermodynamics** is also available on the **Reaction Engineering** or **Chemistry** toolbar.
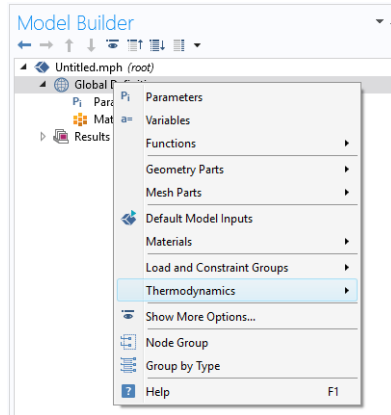
Figure 8-1: The Thermodynamics is always available under Global Definitions.

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 built-in database included with COMSOL Multiphysics.

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 the COMSOL database. You can also edit available species in the database.
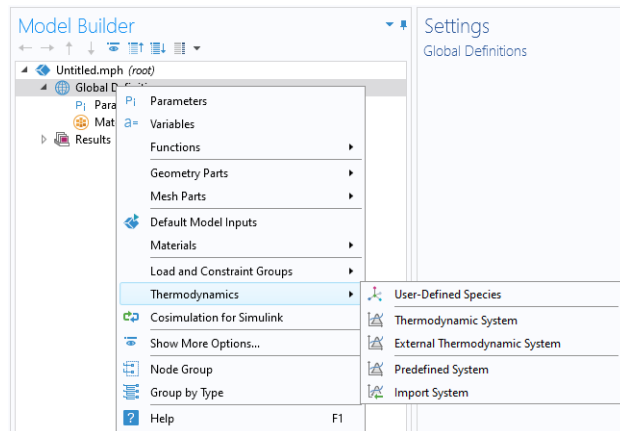
Figure 8-2: Adding Thermodynamic Systems to the Thermodynamics node. Note that external package providers have been installed.

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.
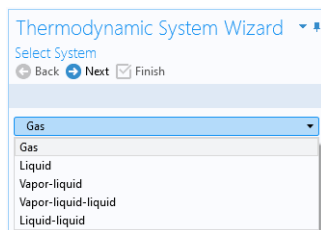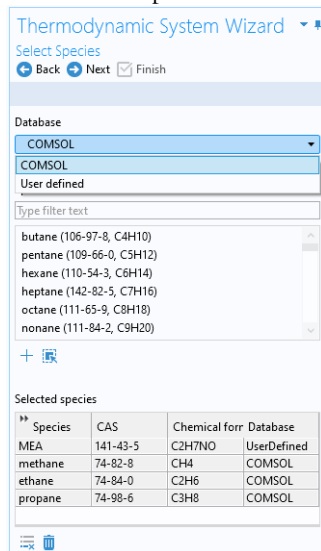
Figure 8-3: Thermodynamic System Wizard: Select System.

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. Using a formula, all species whose chemical formula includes a combination of the given atoms are listed. For example, when searching for ammonia NH3 or H3N can be used.

Select one or more species in the list and click the **Add Selected** button (➕) to add species to the **Selected species** table. You can also press the **Enter** key to add either the

first species in the list, or the species that have been selected. 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 8-4: 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:
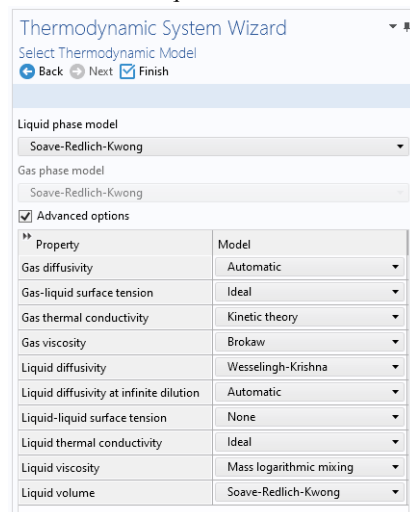
- Gas diffusivity
- Gas thermal conductivity
- Gas viscosity

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 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 8-5: 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 8-6: Thermodynamic System Settings.

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 both gas and liquid phases are available, and the **Liquid phase model** is set to an equation of state, then the **Gas phase model** is set to the same model automatically.

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 8-7 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.

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 8-7: 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).

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 have been changed, select Update From Species for the changes to take effect in the thermodynamic system.
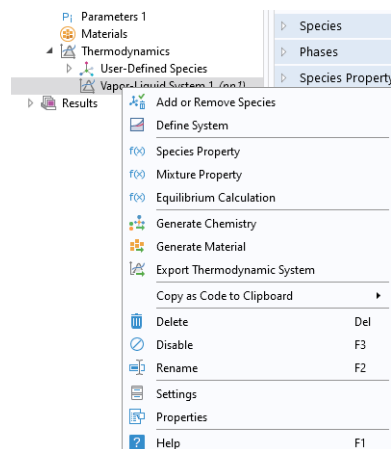
Figure 8-8: Modifying the species and phases of a thermodynamic system.

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 (≡ₓ).

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. Thermodynamics in COMSOL Multiphysics 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 more than 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 8-2). 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, and so on, are available in the **Thermodynamic System Wizard** (Figure 8-9). 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.
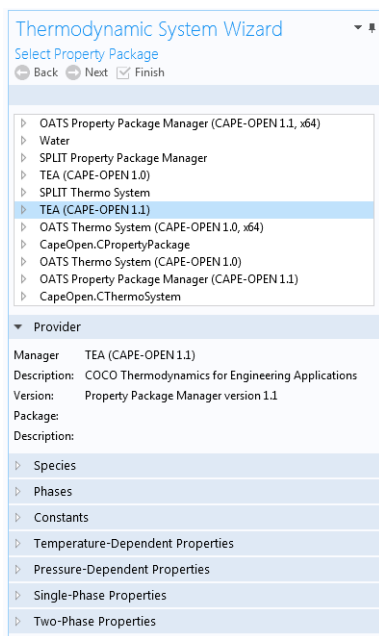
Figure 8-9: Available external thermodynamic systems. Use the Thermodynamic System Wizard to browse the contents of the installed external thermodynamic systems on your system. The example shows the packages shipped with the COCO provider.

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 8-10: 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.
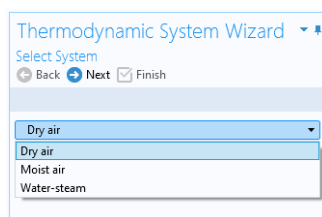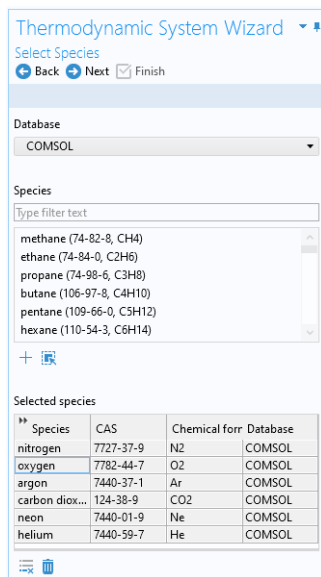
Figure 8-11: Thermodynamic System Wizard: Select Predefined System.

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 (≡ₓ) or the Remove All button (🗑), both located below the table. Click the **Next** button (➡) to proceed to the next step in the wizard.

Figure 8-12: 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.

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 8-8) 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 8-2). Use the **Select File** window to navigate to a thermodynamic system file and click **Open**.

It is possible to manually modify the species properties, such as parameters and temperature-dependent functions, in the created Thermodynamic System by using **Export Thermodynamic System** and **Import Thermodynamic System**. In the saved xml file from **Export thermodynamic system**, there are all parameters and temperature-dependent properties for species, which 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 $f(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3$ 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 8-1: 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

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. The second-order derivatives with respect to temperature and pressure are available for property functions of density and molar volume.

Right-click the relevant **Thermodynamic System** node (see Figure 8-8), **Predefined System** node, or the relevant **External Thermodynamic System** node, and select **Species Property** (f(x)) 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 phase.

Figure 8-13: 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 8-14: Species Property Wizard; Select Phase.

Note that for parameters (constants) this step is skipped.

Click the **Next** button (➡) to proceed to the next step, selecting the species.

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 Species Property Overview in the wizard.
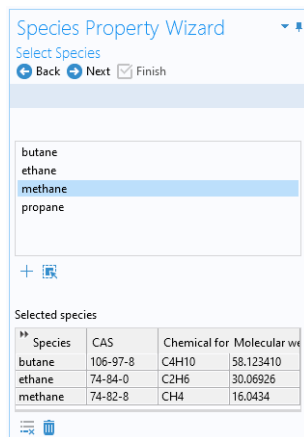
Figure 8-15: Species Property Wizard; the Select Species step.

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**.
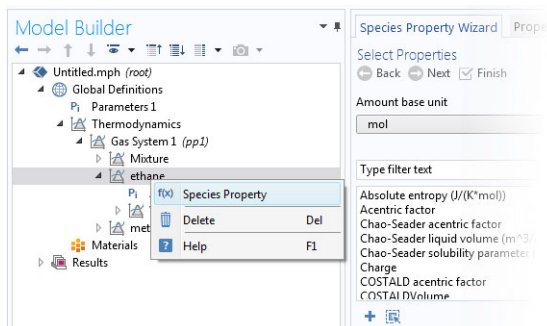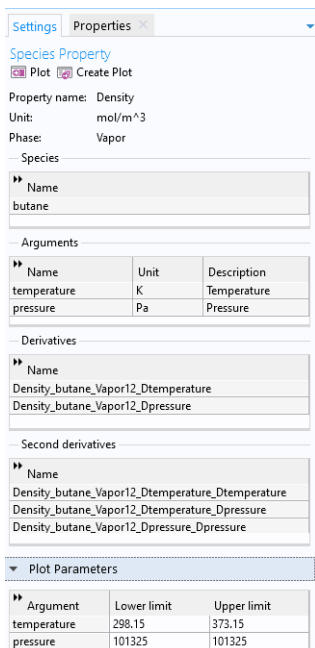
Figure 8-16: Create a Species Property from an existing species node.

Selecting a **Species Property** node shows the settings for such property.

Figure 8-17: 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.
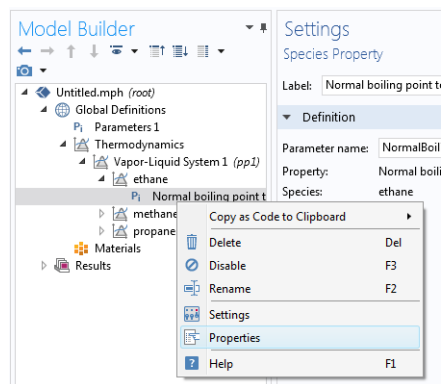
Figure 8-18: Show constant and temperature dependent properties references for species functions.

The reference for the constant or temperature dependent property is available in the **Comments** field in the **Node Properties** section.
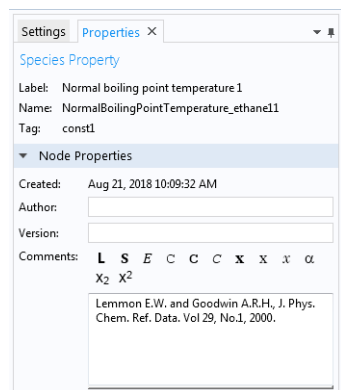
Figure 8-19: Properties window for species function.

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. The second-order derivatives with respect to temperature and pressure are available for property functions of density and molar volume.

Right-click the relevant **Thermodynamic System** node (see Figure 8-8), **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 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**.
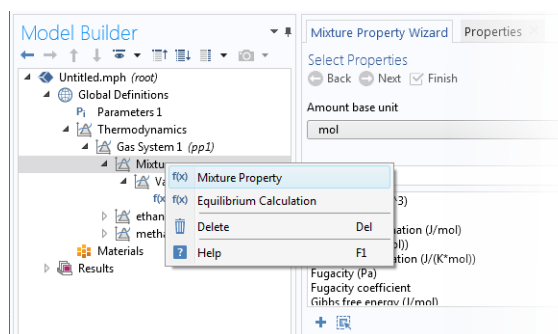
Figure 8-20: Mixture properties can be created by right-clicking a Mixture node under a thermodynamic system.

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. Thermodynamics in COMSOL Multiphysics 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 8-8), **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
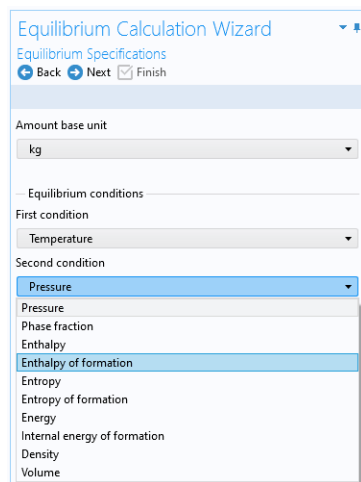
Select one or more of the species available in the thermodynamic system and use the **Add Selected** button (+) to add them to the **Selected species** table. Click the **Next** button (⬄) to proceed to the next step in the wizard.

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 8-21: 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 phenomenon 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 8-20).

SETTINGS

Selecting an **Equilibrium Calculation** node displays the settings including the property functions, see Figure 8-22.

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 8-22: Settings window; Equilibrium calculation.

Generate Chemistry

The Chemistry 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 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 in Chemistry. This means that the species name could be different in Thermodynamics and Chemistry for a 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 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 set up. The material node can include properties such as the density, heat capacity, heat capacity ratio, thermal conductivity, viscosity, and the diffusivity. Two types of property functions can be used, either functions from the underlying thermodynamics 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 8-23: 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

$$\alpha_{iso} = -\frac{1}{\rho}\frac{\partial\rho}{\partial T} \tag{8-1}$$

For a gas phase material, the speed of sound c, and the isentropic compressibility χ_f are also defined as

$$c = \sqrt{\gamma\frac{\partial p}{\partial\rho}}, \qquad \chi_f = \frac{1}{\gamma\rho}\frac{\partial\rho}{\partial p} \tag{8-2}$$

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 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 are 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 functions. 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 and pressure ranges 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.

> [!] The 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.
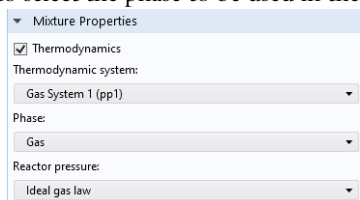
Mixture Properties

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 8-24: 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.
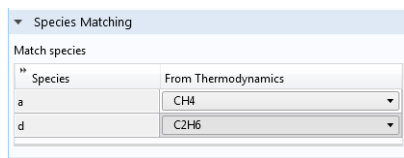
Figure 8-25: Matching the species in Reaction Engineering to those in the corresponding thermodynamic system.

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.
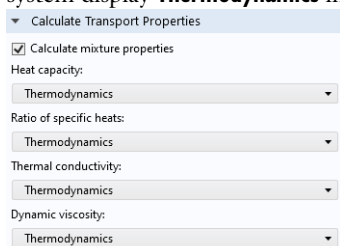
Figure 8-26: Select the Calculate mixture properties check box when coupled to a thermodynamic system.

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.
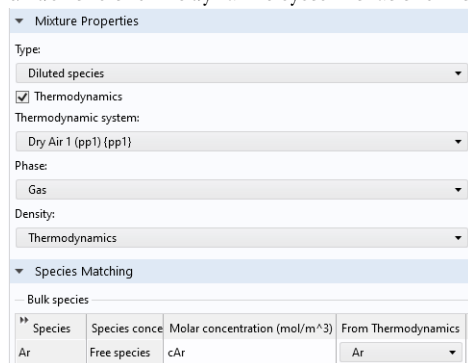
Species Matching

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 8-27: 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 8-26.

MIXTURE PROPERTY DEFINITIONS WHEN COUPLING TO THERMODYNAMICS

When all species in a physics interface (**Reaction Engineering** or **Chemistry**) 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 $Z_{\mathrm{mix}}(T, P, n_1, ..., n_m)$, which denotes a generic extensive mixture property for a mixture of m number of species. The property function's arguments are the temperature T, the 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

$$Z_{\mathrm{mix}} = \sum_{i=1}^{m} n_i \bar{Z}_i \tag{8-3}$$

where $\bar{Z}_i$ is the partial molar of species i:

$$\bar{Z}_i = \left(\frac{\partial Z_{\mathrm{mix}}(T, P, n_1, n_2, ..., n_m)}{\partial n_i} \right)_{T, P, n_{j \neq i}} \tag{8-4}$$

The definition of partial molar properties can be rewritten using mole fraction derivatives as:

$$\bar{Z}_i(T, P, n_1, ..., n_m) = \bar{Z}_i(T, P, x_1, ..., x_m) = \tag{8-5}$$

$$\left(Z_{\mathrm{mix}}(T, P, x_1, ..., x_m) + \left(\frac{\partial Z_{\mathrm{mix}}(T, P, x_1, ..., x_m)}{\partial x_i} \right)_{T, P, x_{i \neq j}} \right.$$

$$\left. - \sum_{i=1}^{m} \left(x_i \left(\frac{\partial Z_{\mathrm{mix}}(T, P, x_1, ..., x_m)}{\partial x_i} \right)_{T, P, x_{i \neq j}} \right) \right)$$

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:

$$Z_{\mathrm{mix}} = \sum_{i=1}^{m} n_i Z_i(T, P) \tag{8-6}$$

using the pure species properties $Z_i = Z_{\mathrm{mix}}(T, P, x_i = 1, 0, ..., 0)$.

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 8-28 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.
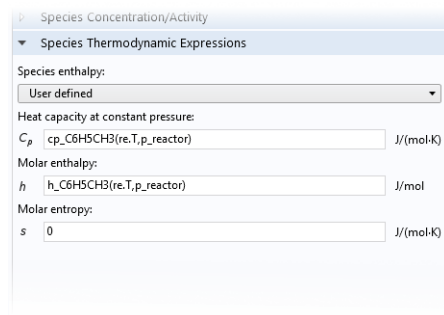
Figure 8-28: The enthalpy and heat capacity of toluene are evaluated using property calculations through a thermodynamics system. In this case, the functions are temperature and pressure dependent properties for a pure component.

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** or **Chemistry** interface, choose **User-Defined Species** from the **Thermodynamics** section of the **Reaction Engineering** or **Chemistry** toolbar.
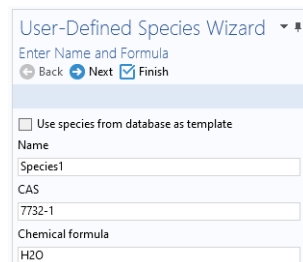
The **User-Defined Species Wizard** contains the following steps:

1 Enter Name and Formula
2 Enter Parameters

3 Define Properties

Enter the **Name**, **CAS** number, and the **Chemical formula** for the new species.

Figure 8-29: 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 8-30: 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 8-31: 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 8-32: 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.

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 8-33: 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

$$f(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3 \qquad (8-7)$$

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 8-34: 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 8-35 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 8-35: 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

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

$$Z \equiv \frac{PV}{RT} = f_v(V, T) \tag{8-8}$$

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 comparison of different cubic EOS models can be found in Ref. 2 and Ref. 3.

The equations 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

$$P = \frac{RT}{V} \tag{8-9}$$

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. 5 is given by

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V^2 + 2bV - b^2} \tag{8-10}$$

where for species i,

$$a_i = \Omega_A \frac{R^2 T_c^2}{P_c} \tag{8-11}$$

$$b_i = \Omega_B \frac{RT_c}{P_c} \tag{8-12}$$

$$\Omega_A = \frac{1}{3} + \frac{1}{3}\Omega_B(4 + 10\Omega_B) \tag{8-13}$$

$$\Omega_B = \left(\beta - \frac{63}{1024\beta} - 0.03125\right) \tag{8-14}$$

$$\beta = \left(\frac{351}{32768} + \frac{27}{2048}\sqrt{2}\right)^{\frac{1}{3}} \tag{8-15}$$

The alpha function, α_i, is given by

$$\alpha_i = [1 + (0.37464 + 1.54226\omega_i - 0.26992\omega_i^2)(1 - \sqrt{T_{r,i}})]^2 \tag{8-16}$$

For mixtures

$$a\alpha = \sum_i \sum_j x_i x_j (1 - k_{PR,i,j}) \sqrt{(a\alpha)_i (a\alpha)_j} \tag{8-17}$$

$$b = \sum_i x_i b_i \tag{8-18}$$

The binary interaction parameters (BIPs), k_{PR}, are symmetric with zeros in the diagonal:

$$k_{PR} = k_{PR,i,j} \tag{8-19}$$

$$k_{PR,i,j} = 0 \tag{8-20}$$

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 modification (Ref. 6) of the Peng–Robinson model, the alpha function, α_i, is replaced by

$$\alpha_i = T + R^{(N_i(M_i - 1))} \exp(L_i(1 - T_{r,i}^{N_i M_i})) \tag{8-21}$$

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. 7 is given by

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)} \tag{8-22}$$

with

$$\alpha = \frac{1}{\sqrt{T}} \tag{8-23}$$

and for the pure species i,

$$a_i = \Omega_A \frac{R^2 T_c^{2.5}}{P_c} \tag{8-24}$$

$$b_i = \Omega_B \frac{RT_c}{P_c} \tag{8-25}$$

$$\Omega_A = \frac{1}{3} + \frac{1}{3}\Omega_B(3 + 3\Omega_B) \tag{8-26}$$

$$\Omega_B = \frac{1}{27}2^{\frac{1}{3}}27^{\frac{2}{3}} - \frac{1}{3} \tag{8-27}$$

For mixtures

$$a = \sum_i \sum_j x_i x_j (1 - k_{\text{SRK},i,j}) \sqrt{a_i a_j} \tag{8-28}$$

$$b = \sum_i x_i b_i \tag{8-29}$$

The binary interaction parameters, k_{SRK}, are symmetric with zero in the diagonal:

$$k_{\text{SRK},\mathbf{i,j}} = k_{\text{SRK},\mathbf{j,i}} \tag{8-30}$$

$$k_{\text{SRK},\mathbf{i,j}} = 0 \tag{8-31}$$

If a value is missing for $k_{\text{SRK},i,j}$ 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 8-22 modified by Soave Ref. 8, where for pure species i, the alpha function is modified to

$$\alpha_i = [1 + (0.480 + 1.574\omega_i - 0.176\omega_i^2)(1 - \sqrt{T_{r,i}})]^2 \tag{8-32}$$

Soave–Redlich–Kwong (Graboski–Daubert)
The Graboski and Daubert Ref. 9 modification of the Soave–Redlich–Kwong equation of state replaces alpha function by

$$\alpha_i = [1 + (0.48508 + 1.55174\omega_i - 0.1561\omega_i^2)(1 - \sqrt{T_{r,i}})]^2 \tag{8-33}$$

except for H_2, where it is replaced by

$$\alpha_{H_2} = 1.202 \exp(-0.30228 T_{r,H_2}) \tag{8-34}$$

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. 10 - Ref. 12. The correlations are valid in the following ranges:

$$273.15 \text{ K} \leq T \leq 1073.15 \text{ K} \qquad\qquad p \leq 100 \text{ MPa} \tag{8-35}$$

$$1073.15 \text{ K} \leq T \leq 2273.15 \text{ K} \qquad\qquad p \leq 50 \text{ MPa} \tag{8-36}$$

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 the COMSOL database.

LIQUID PHASE MODELS

Activity coefficient models
Activity coefficient models are used to describe liquid mixtures at low to moderate pressures and temperatures where the equations of state are inadequate. When using activity coefficient models, the partial fugacity for species i in the liquid phase is defined as

$$\hat{f}_{i,l} = x_i \gamma_i \phi_{i,sat} P_{i,\text{sat}} F_i \tag{8-37}$$

which yields

$$\hat{\phi}_{i,l} = \gamma_i \phi_{i,\text{sat}} \frac{P_{i,\text{sat}}}{P} F_i \tag{8-38}$$

where the activity coefficient, γ_i, describes the nonideal liquid phase and $\hat{\phi}_{i,\text{sat}} P_{i,\text{sat}}$ 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

$$F_i = \exp\left(\int_{P_{i,sat}}^{P} \frac{V_{i,l}}{RT} dp\right) \tag{8-39}$$

For an incompressible liquid, an approximation of the Poynting correction can be done according to

$$F_i \approx \exp\left(\frac{V_{i,l}}{RT}(P - P_{i,\text{sat}})\right) \tag{8-40}$$

The Poynting correction can often be ignored for moderate pressure. Hence, Equation 8-38 can be expressed as

$$\hat{\phi}_{i,l} = \gamma_i \phi_{i,sat} \frac{P_{i,\text{sat}}}{P} \tag{8-41}$$

If the vapor phase is considered ideal, then $\phi_{i,\text{sat}} = 1$ and the above equation reduces to

$$\hat{\phi}_{i,l} = \gamma_i \frac{P_{i,\text{sat}}}{P} \tag{8-42}$$

This reduction can be selected explicitly in case the vapor phase is not ideal.

The logarithmic transformation of Equation 8-38 is:

$$\ln\hat{\phi}_{i,l} = \ln\gamma_i + \ln\phi_{i,\text{sat}} + \ln P_{i,\text{sat}} - \ln P + \ln F_i \tag{8-43}$$

Ideal Solution
For an ideal solution the activity coefficient is equal to one, which gives:

$$\ln\gamma_i = 0 \tag{8-44}$$

Regular Solution

The Scatchard–Hildebrand equation Ref. 14 for a nonpolar mixture is

$$\ln\gamma_i = \frac{V_i(\delta_i - \delta_{av})^2}{RT} \tag{8-45}$$

where V_i is species molar volume and δ_i is species solubility parameter, and δ_{av} is

$$\delta_{av} = \frac{\sum_i (x_i V_i \delta_i)}{\sum_i (x_i V_i)} \tag{8-46}$$

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:

$$\delta_i \equiv \sqrt{\frac{\Delta H_{vap,i}}{V_{i,l,b}}} \tag{8-47}$$

Extended Regular Solution

The extended Scatchard–Hildebrand equation adds the Flory and Huggins correction to the regular solution model Ref. 16:

$$\ln\gamma_i = \frac{V_i(\delta_i - \delta_{av})^2}{RT} + \ln(\theta_i) + 1 - \theta_i \tag{8-48}$$

where

$$\theta_i = \frac{V_i}{\sum_i (x_i V_i)} \tag{8-49}$$

Wilson

Wilson Ref. 17 derived his activity coefficient model from a consideration of probabilities of neighboring molecules in a liquid

$$\ln \gamma_i = 1 - \sum_j \left(\frac{x_j \Lambda_{j,i}}{\sum_k x_k \Lambda_{j,k}} \right) - \ln \left(\sum_j x_j \Lambda_{i,j} \right) \tag{8-50}$$

$$\Lambda_{i,j} = \frac{V_{w,j}}{V_{w,i}} \exp\left(-\frac{\lambda_{i,j}}{T}\right) \tag{8-51}$$

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

$$\lambda_{i,i} = 0 \tag{8-52}$$

$$\Lambda_{i,i} = 1 \tag{8-53}$$

NRTL

Renon and Prausnitz (Ref. 18) formulated a three parameter activity coefficient model that is able to describe liquid-liquid equilibrium; the nonrandom two-liquid (NRTL) model:

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{j,i} G_{j,i}}{\sum_j x_j G_{j,i}} + \sum_j \left(\frac{x_j G_{j,i}}{\sum_k x_k G_{k,j}} \left(\tau_{i,j} - \frac{\sum_k x_k \tau_{k,j} G_{k,j}}{\sum_k x_k G_{k,j}} \right) \right) \tag{8-54}$$

$$\tau_{i,j} = \frac{A_{i,j}}{T} \tag{8-55}$$

$$G_{i,j} = \exp(-\alpha_{i,j} \tau_{i,j}) \tag{8-56}$$

The three parameters are $A_{i,j}$, $A_{j,i}$, and $\alpha_{i,j}$. A more general form is implemented here:

$$\tau_{i,j} = \frac{A_{i,j}}{T} + B_{i,j} \tag{8-57}$$

$$G_{i,j} = \exp(\beta_{i,j} - \alpha_{i,j} \tau_{i,j}) \tag{8-58}$$

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).

$$A_{i,i} = 0 \tag{8-59}$$

$$B_{i,i} = 0 \tag{8-60}$$

$$\alpha_{i,i} = 0 \tag{8-61}$$

$$\alpha_{j,i} = \alpha_{i,j} \tag{8-62}$$

$$\tau_{i,i} = 0 \tag{8-63}$$

$$G_{i,i} = 1 \tag{8-64}$$

$$\beta_{i,i} = 0 \tag{8-65}$$

UNIQUAC

Abrams and Prausnitz followed up with another two-liquid model known as Universal Quasi Chemical equation (UNIQUAC) (see Ref. 19), which is formulated in terms of two activity coefficients:

$$\ln \gamma_i = \ln \gamma_{i, \text{comb}} + \ln \gamma_{i, \text{res}} \tag{8-66}$$

The first term is the combinatorial part contributes to the Gibbs free energy originating from size and shape effects as

$$\ln \gamma_{i, \text{comb}} = 1 - \phi_i + \ln \phi_i - \frac{z}{2} q_i \left(1 + \frac{\phi_i}{\theta_i} + \ln\left(\frac{\phi_i}{\theta_i}\right) \right) \tag{8-67}$$

and the second term is the residual part from chemical interactions between the molecules,

$$\ln\gamma_{i,\,\mathrm{res}} = q_i\left[1 - \ln\left(\frac{\sum\limits_{j} x_j q_j \tau_{j,\,i}}{\sum\limits_{j} x_j q_j}\right) - \sum_{j}\frac{x_j q_j \tau_{j,\,i}}{\sum\limits_{k} x_j q_j \tau_{k,\,j}}\right] \qquad (8\text{-}68)$$

where

$$\phi_i = \frac{r_i}{\sum\limits_{j} x_j r_j} \qquad (8\text{-}69)$$

$$\theta_i = \frac{q_i}{\sum\limits_{j} x_j q_j} \qquad (8\text{-}70)$$

$$\tau_{i,j} = \exp\left(\frac{-\Delta E_{i,j}}{T}\right) \qquad (8\text{-}71)$$

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.

$$\Delta E_{i,i} = 0 \qquad (8\text{-}72)$$

$$\tau_{i,i} = 1 \qquad (8\text{-}73)$$

The volume parameters, r_i, and surface area parameters, q_i, are model-specific parameters for each species. If the parameters are not specified, they can be derived from the van der Waals volume, $V_{\mathrm{VDW},i}$, and area, $A_{\mathrm{VDW},i}$, respectively

$$r_i = \frac{V_{\mathrm{VDW},i}}{0.01517 \cdot 10^{-3}} \qquad (8\text{-}74)$$

$$q_i = \frac{A_{\mathrm{VDW},i}}{2.5 \cdot 10^{-5}} \qquad (8\text{-}75)$$

For all species r_i or $V_{\mathrm{VDW},i}$ and q_i or $A_{\mathrm{VDW},i}$ must be specified.

UNIFAC

The UNIQUAC Functional-group Activity Coefficients (UNIFAC; see Ref. 20) 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 8-66. The combinatorial part follows from equation Equation 8-67, where

$$r_i = \sum_k \nu_{k,i} r_k \tag{8-76}$$

$$q_i = \sum_k \nu_{k,i} q_k \tag{8-77}$$

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 8-66 is calculated from a summation over functional groups:

$$\ln \gamma_{i,\,\mathrm{res}} = \sum_k \nu_{k,i} (\ln \gamma_{k,\,\mathrm{res}} - \ln \gamma_{i,k,\,\mathrm{res}}) \tag{8-78}$$

The values for $\ln(\gamma_{k,\mathrm{res}})$ are calculated from the mixture containing all species at a specified composition x. The values for $\ln(\gamma_{i,k,\mathrm{res}})$ are calculated for a mixture of group k considering only pure species i. Both are defined, for functional group k, by

$$\ln \gamma_{k,\,\mathrm{res}} = q_k \left(1 - \ln \left(\frac{\sum_l x_l q_l \tau_{l,k}}{\sum_l x_l q_l} \right) - \sum_j \frac{x_l q_l \tau_{k,l}}{\sum_m x_l q_l \tau_{m,l}} \right) \tag{8-79}$$

where x_l and x_m are the compositions of functional group l and m in the mixture

$$x_m = \frac{\sum_i x_i \nu_{m,i}}{\sum_i \left(x_i \sum_k \nu_{k,i} \right)} \tag{8-80}$$

For the calculation of a pure species' i residual activity we get:

$$x_m = \frac{v_{m,i}}{\sum_k v_{k,i}} \tag{8-81}$$

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

$$\tau_{k,m} = \exp\left(-\frac{A_{k,m}}{T}\right) \tag{8-82}$$

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. 21 through Ref. 26), with added groups from Balslev and Abildskov (Ref. 27) 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. 13 correlates liquid phase partial coefficients for pure species, for use of hydrogen and hydrocarbon mixtures at elevated pressure and temperatures. It is expressed by

$$\ln \phi_{i,l} = \ln \gamma_i + \ln \phi_{i,l,0} \tag{8-83}$$

The activity is based on the Scatchard–Hildebrand equation Ref. 14 and presented in Equation 8-45 to Equation 8-47. 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 8-80, 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

$$\log \phi_{i,l,0} = \log \phi_{i,l,1} + \omega_i \log \phi_{i,l,2} \tag{8-84}$$

$$\log\phi_{i,l,1} = A_{i,0} + \frac{A_{i,1}}{T_{r,i}} + A_{i,2}T_{r,i} + A_{i,3}T_{r,i}^2 + A_{i,4}T_{r,i}^3 \tag{8-85}$$

$$+(A_{i,7}T_{r,i}^2 + A_{i,6}T_{r,i} + A_{i,5})P_{r,i} + (A_{i,9}T_{r,i} + A_{i,8})P_{r,i}^2 - \log P_{r,i}$$

$$\log\phi_{i,l,2} = A_{i,10} + \frac{A_{i,12}}{T_{r,i}} + A_{i,11}T_{r,i} + A_{i,13}T_{r,i}^3 + A_{i,14}(P_{r,i} - 0.6) \tag{8-86}$$

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. 15 and given in Table 8-2.

TABLE 8-2: 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 systems that include 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 8-109 to Equation 8-118.

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:

$$\rho_l = \frac{1}{V_l} \tag{8-87}$$

Using a cubic equation of state, the solution has 1, 2, or 3 different roots for the volume. The liquid density is defined as the root producing the highest density, and the vapor density as the root producing the lowest density.

Equation of State

When an equation of state is selected as the liquid phase model, the liquid volume is by default set to be calculated using the same equation of state model. The other liquid volume models; Ideal Mixture, COSTALD, and Rackett are also available.

Note, the vapor phase model and the liquid volume cannot use different equation of state models.

Ideal Mixture

For an ideal mixture the liquid volume is computed from the pure species densities (corresponding to the saturated liquid density):

$$V_{l,m} = \sum_i \frac{x_i}{\rho_{i,l}} \tag{8-88}$$

In this case the pure species densities corresponds to the saturated liquid density, which is available as a temperature dependent correlation for all species in the built-in database.

COSTALD

Hankinson and Thomson Ref. 28 presented the Corresponding States Liquid Density (COSTALD) equation as

$$\frac{V}{V_{mix}} = V_{r,ref}(1 - \omega V_{r,\delta}) \tag{8-89}$$

$$V_{r, ref} = 1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + c(1 - T_r) + d(1 - T_r)^{4/3} \qquad (8\text{-}90)$$

$$V_{r, \delta} = \frac{e + fT_r + gT_r^2 + hT_r^3}{T_r - 1.00001} \qquad (8\text{-}91)$$

$$V_{mix} = \frac{1}{4}\left(\sum_i x_i V_i + 3\left(\sum_i x_i V_i^{2/3} \right)\left(\sum_i x_i V_i^{1/3} \right) \right) \qquad (8\text{-}92)$$

$$T_c = \frac{\left(\sum_i x_i \sqrt{T_{c,i} V_i} \right)^2}{V_{mix}} \qquad (8\text{-}93)$$

$$T_r = \begin{cases} \dfrac{T}{T_c} & T < T_c \\ 1 & T \geq T_c \end{cases} \qquad (8\text{-}94)$$

$$\omega = \sum_i x_i \omega_i \qquad (8\text{-}95)$$

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

$$\begin{aligned} V_i = {} & 5.385\, V_{VDW,i} - 5.1022 V_{VDW,i}^2 + 79.524 V_{VDW,i}^3 \\ & - 99.316 V_{VDW,i}^4 + 100.88 V_{VDW,i}^5 - 1152.7 V_{VDW,i}^6 \end{aligned} \qquad (8\text{-}96)$$

otherwise, it can be set equal to the critical volume as

$$V_i = V_{c,i} \qquad (8\text{-}97)$$

If the COSTALD acentric factor, ω_i is not specified, it can be set equal to the generic acentric factor for species i. A critical temperature, $T_{c,i}$ must be specified for all species.

The correlation parameter values are:

TABLE 8-3: REDUCED VOLUME CORRELATION PARAMETERS IN COSTALD.

a	-1.52816	e	-0.296123
b	1.43907	f	0.386914

TABLE 8-3: REDUCED VOLUME CORRELATION PARAMETERS IN COSTALD.

c	-0.81446	g	-0.0427258
d	0.190454	h	-0.0480645

Rackett

The Rackett equation Ref. 29 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:

$$V_l = \left(R \sum_i \frac{x_i T_{c,i}}{(MW)_i P_{c,i}} \right) \left(\sum_i Z_{r,i} \right)^{(1 + (1 - T_r^2)^{2/7})} \left(\sum_i x_i (MW)_i \right) \qquad (8\text{-}98)$$

$$T_c = \sum_i x_i T_{c,i} \qquad (8\text{-}99)$$

$$T_r = \begin{cases} \dfrac{T}{T_c} & T < T_c \\ 1 & T \geq T_c \end{cases} \qquad (8\text{-}100)$$

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:

$$Z_{r,i} = Z_{c,i} \qquad (8\text{-}101)$$

Selecting the Right Thermodynamic Model

Which thermodynamic model is the most appropriate depends on a number of things, for example the nature of the properties to be used, the operational pressure and temperature, and not least the availability of the required model parameters. One general introduction to how to select thermodynamic models, as well as estimating missing parameters and validating properties can be found in Ref. 77.

Below is a decision tree that can be used as a guide for choosing the thermodynamic model:
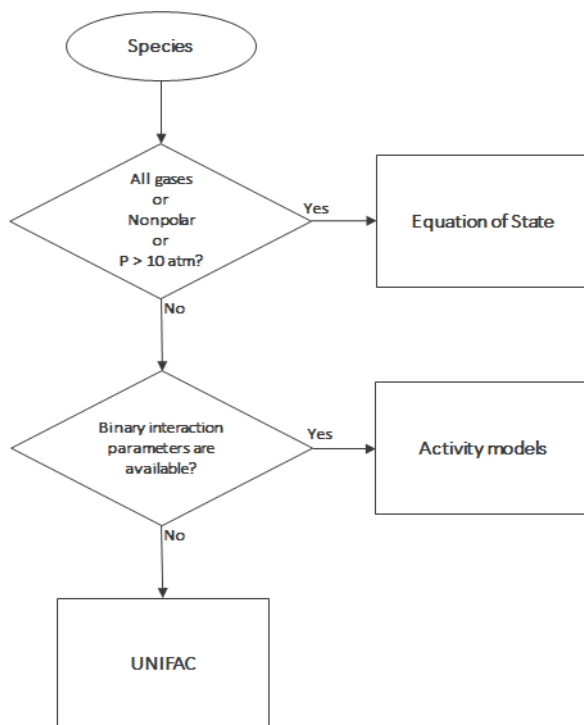
Figure 8-36: Decision tree to select thermodynamics model.

Species Property References

All references used for the included constants and temperature-dependent properties are available in the database file. 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

$$\rho = \frac{1}{V} \tag{8-102}$$

The partial fugacity coefficients

$$\ln \hat{\phi}_i = 0 \tag{8-103}$$

The ideal gas enthalpy for mixture

$$H_{ig} = \sum_i x_i \left(H_{i,\,ig,\,T_{ref}} + \int_{T_{ref}}^{T} C_{P,\,i,\,ig} dT \right) \tag{8-104}$$

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

$$S_{ig} = \sum_i x_i \left(S_{i,\,ig,\,T_{ref}} - R \ln x_i + \int_{T_{ref}}^{T} \frac{C_{P,\,i,\,ig}}{T} dT \right) - R \ln \left(\frac{P}{P_{ref}} \right) \tag{8-105}$$

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

$$G_{ig} = H_{ig} - T S_{ig} \tag{8-106}$$

Equation of State

The equation of state determines V at given x, T, and P. Density can be expressed as Equation 8-102. The partial fugacity coefficients are derived from

$$\ln \hat{\phi}_i = \frac{1}{RT} \int_0^P \left(\hat{V}_i - \frac{RT}{P} \right) \tag{8-107}$$

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:

$$H = H_{ig} - RT^2 \sum_i x_i \left(\frac{\partial \ln \hat{\phi}_i}{\partial T} \right) \qquad (8\text{-}108)$$

$$S = S_{ig} - R \sum_i x_i \left(\ln \hat{\phi}_i + T \frac{\partial \ln \hat{\phi}_i}{\partial T} \right) \qquad (8\text{-}109)$$

$$G = G_{ig} - RT \sum_i x_i \ln \hat{\phi}_i \qquad (8\text{-}110)$$

Heat Capacity

The heat capacity at constant pressure is calculated from

$$C_P = \left(\frac{\partial H}{\partial T} \right)_{P,x} \qquad (8\text{-}111)$$

It is available when the enthalpy is available. The heat capacity at constant volume is defined by

$$C_v = \left(\frac{\partial H}{\partial T} \right)_{v,x} \qquad (8\text{-}112)$$

The relationship between the heat capacity at constant pressure and constant volume can be expressed as

$$C_p - C_v = T \left(\frac{\partial V}{\partial T} \right)_{P,x} \left(\frac{\partial P}{\partial T} \right)_{v,x} \qquad (8\text{-}113)$$

were v is a function of T and P. A Taylor expansion of v at constant composition gives

$$\Delta v = \left(\frac{\partial V}{\partial T} \right)_{P,x} \Delta T + \left(\frac{\partial V}{\partial P} \right)_{T,x} \Delta P = 0 \qquad (8\text{-}114)$$

Rearranging equations above gives

$$C_v = C_P + \frac{T \left(\frac{\partial V}{\partial T} \right)_{P,x}^2}{\left(\frac{\partial V}{\partial P} \right)_{T,x}} \qquad (8\text{-}115)$$

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 8-113 express as

$$C_p - C_v = R \tag{8-116}$$

Specific heat capacity ratio is defined as

$$\Upsilon = \frac{C_p}{C_v} \tag{8-117}$$

Activity Coefficient Models

The enthalpy, entropy, and Gibbs free energy follow from the activity coefficients and the ideal gas contributions in Equation 8-104 – Equation 8-106. The activity coefficients describe the deviation of chemical potentials from the ideal liquid phase, so heats of vaporization need to be accounted for

$$H = \sum_i x_i \bigg(H_{i,ig,T_{ref}} + \int_{T_{ref}}^{T} C_{P,i,ig} dT - \Delta H_{i,vap} - RT^2 \frac{\partial \ln \gamma_i}{\partial T} \tag{8-118}$$
$$- RT^2 \frac{\partial \ln \hat{\phi}_{i,sat}}{\partial T} \bigg)$$

$$S = \sum_i x_i \bigg(S_{i,ig,T_{ref}} - R\ln x_i + \int_{T_{ref}}^{T} \frac{C_{P,i,ig}}{T} dT - R\ln\bigg(\frac{P_{i,sat}}{P_{ref}}\bigg) \tag{8-119}$$
$$+ \ln \gamma_i + T\frac{\partial \ln \gamma_i}{\partial T} + \ln \hat{\phi}_{i,sat} + T\frac{\partial \ln \hat{\phi}_{i,sat}}{\partial T} + R\frac{\Delta H_{i,vap}}{T} \bigg)$$

$$G = \sum_i x_i \bigg(H_{i,ig,T_{ref}} + \int_{T_{ref}}^{T} C_{P,i,ig} dT - T\bigg(S_{i,ig,T_{ref}} + \tag{8-120}$$
$$\int_{T_{ref}}^{T} \frac{C_{P,i,ig}}{T} dT \bigg) + RT\bigg(\ln x_i + \ln \gamma_i + \ln \hat{\phi}_{i,sat} + \ln \frac{P_{i,sat}}{P_{ref}}\bigg) \bigg)$$

Note that if the vapor phase is ideal, then the saturated fugacity, $\hat{\phi}_{i,sat}$, contribution can be ignored.

Other Properties

Partial fugacity is calculated from

$$\hat{f}_i = x_i \hat{\phi}_i P \tag{8-121}$$

Internal energy is calculated from

$$U = H - PV + \sum_i x_i U_{i,\,ig,\,\text{ref}} \tag{8-122}$$

where $U_{i,ig,\text{ref}}$ is the enthalpy of an ideal gas to the species enthalpy at the selected reference state.

Helmholtz energy is calculated from

$$A = U - TS = G - PV \tag{8-123}$$

The K-values for phases p and q are taken from

$$K_{i,\,p,\,q} = \frac{\hat{\phi}_{i,\,q}}{\hat{\phi}_{i,\,p}} \tag{8-124}$$

If only liquid phases are defined, the K-value calculation is reduced to

$$K_{i,\,p,\,q} = \frac{\gamma_{i,\,q}}{\gamma_{i,\,p}} \tag{8-125}$$

$$M_{\text{mix}} = \sum_i x_i M_i \tag{8-126}$$

Standard Enthalpy of Formation and Absolute Entropy Terms

Formation terms are not included in the enthalpy, entropy, or 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

$$\Delta H_{\text{reac,ref}} = \sum_i \nu_i (\Delta H_{f,\,\text{ref}}) \tag{8-127}$$

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:

$$H_F = H + \sum_i x_i \Delta H_{f,\,i,\,\text{ref}} \tag{8-128}$$

$H_{f,i,\text{ref}}$ 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

$$S_F = S + \sum_i x_i S_{\text{abs}, i} \qquad (8\text{-}129)$$

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 8-129 and in consequence Gibbs free energy Equation 8-110 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:

$$S_i = \Delta S_{f,i} = \sum_j \nu_j S_{\text{abs}j} \qquad (8\text{-}130)$$

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

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3 \qquad (8\text{-}131)$$

$$\Delta S_{f, NH_3} = 2S_{\text{abs}, NH_3} - (S_{\text{abs}, N_2} + 3S_{\text{abs}, H_2}) \qquad (8\text{-}132)$$

The values from RHS of Equation 8-132 can be extracted from COMSOLThermoDB. This value should be used in Equation 8-128 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, $H_{i,\text{ref}}$, entropy, $S_{i,\text{ref}}$, and internal energy, $U_{i,\text{ref}}$, 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:

$$\lambda_v = \sum_i x_i \lambda_{i,v} + \Delta\lambda_{v,P} \tag{8-133}$$

The pressure correction $\Delta\lambda_{v,P}$ is calculated from the method of Stiel and Thodos, see Ref. 30, 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

$$\Delta\lambda_{v,P} = \frac{P_c^{2/3}}{\sqrt{\bar{M}} T_c^{1/6} Z_c^5} A(\exp((B\rho_r) + C)) \tag{8-134}$$

$$\rho_r = \frac{\rho}{\rho_c} \tag{8-135}$$

$$\rho_c = \frac{1}{V_c} \tag{8-136}$$

The mixing rules are as suggested by Yorizane, see Ref. 31:

$$V_c = \sum_i x_i \sum_j x_j V_{c,i,j} \tag{8-137}$$

$$T_c = \frac{\sum_i x_i \sum_j x_j V_{c,i,j} T_{c,i,j}}{V_c} \tag{8-138}$$

$$\omega = \sum_i x_i \omega_i \tag{8-139}$$

$$Z_c = 0.291 - 0.08\omega \tag{8-140}$$

$$P_c = \frac{RT_c Z_c}{V_c} \tag{8-141}$$

$$M = \sum_i x_i M_i \tag{8-142}$$

where the binary constants are

$$V_{c,i,j} = \frac{1}{8}(V_{c,i}^{1/3} + V_{c,j}^{1/3})^3 \tag{8-143}$$

$$T_{c,i,j} = \sqrt{T_{c,i} T_{c,j}} \tag{8-144}$$

The Stiel and Thodos coefficients are

TABLE 8-4: PRESSURE CORRECTION PARAMETERS.

	A	B	C
$\rho_r < 0.5$	A_1=2.702E8	B_1=0.535	C_1=-1
$0.5 \le \rho_r < 2.0$	A_2=2.528E8	B_2=0.670	C_2=-1.069
$\rho_r \ge 2.0$	A_3=0.574E8	B_3=1.155	C_3= 2.016

However, in order to ensure 0th-order continuity at $\rho_r = 0.5$ and $\rho_r = 2.0$, the following coefficients for $0.5 \leq \rho_r < 2.0$ are recalculated from

$$A_2 = -\frac{A_1 C_1 + A_1 \exp(0.5 \ B_1) - A_3 C_3 - A_3 \exp(2.0 \ B_3)}{\exp(2.0 \ B_2) - \exp(0.5 \ B_1)} \tag{8-145}$$

$$C_2 = -\frac{A_1 C_1 \exp(2.0 \ B_2) + A_1 \exp(0.5 \ B_1)\exp(2.0 \ B_2)}{A_1 C_1 + A_1 \exp(0.5 \ B_1) - A_3 C_3 - A_3 \exp(2.0 \ B_3)} \tag{8-146}$$
$$-\frac{A_3 C_3 \exp(2.0 \ B_2) + A_3 \exp(0.5 \ B_2)\exp(2.0 \ B_3)}{A_1 C_1 + A_1 \exp(0.5 \ B_1) - A_3 C_3 - A_3 \exp(2.0 \ B_3)}$$

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. 32) provided an equation for the interaction parameters of the method of Wassiljewa (see Ref. 33) based on the kinetic theory, to provide mixture thermal conductivity from pure species values

$$\lambda_v = \sum_i \left(\frac{x_i \lambda_{i,v}}{\sum_j x_j \phi_{i,j}} \right) + \Delta\lambda_{v,P} \tag{8-147}$$

$$\phi_{i,j} = \frac{1}{4}\left(1 + \sqrt{\frac{\eta_{i,v}}{\eta_{j,v}}\left(\frac{M_j}{M_i}\right)^{3/4}\left[\frac{T + \left(\frac{3}{2}\right)T_{b,i}}{T + \left(\frac{3}{2}\right)T_{b,j}}\right]} \right)^2 \left(\frac{T + \sqrt{\left(\frac{9}{4}\right)T_{b,i}T_{b,j}}}{T + \left(\frac{3}{2}\right)T_{b,i}} \right) \tag{8-148}$$

where the pressure correction $\Delta\lambda_{v,P}$ is calculated from Equation 8-134. 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. 34 which is valid in the following range:

$$273.15 \text{ K } \leq T \leq 773.15 \text{ K} \qquad\qquad p \leq 100 \text{ MPa} \qquad\qquad (8\text{-}149)$$

$$773.15 \text{ K } \leq T \leq 923.15 \text{ K} \qquad\qquad p \leq 70 \text{ MPa} \qquad\qquad (8\text{-}150)$$

$$923.15 \text{ K } \leq T \leq 1073.15 \text{ K} \qquad\qquad p \leq 40 \text{ MPa} \qquad\qquad (8\text{-}151)$$

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

$$\lambda_{l,m} = \sum_i x_i \lambda_{i,l} \qquad\qquad (8\text{-}152)$$

The pressure dependence is based on the work of Missenard (Ref. 51) where

$$\frac{\lambda_{l,m,P}}{\lambda_{l,m}} = 1 + Q P_r^{0.7} \qquad\qquad (8\text{-}153)$$

where Q is correlated as

$$Q = -0.013693477 + 0.057427673 T_r + 0.001617831 (T_r)(\ln P_1) \qquad (8\text{-}154)$$

and the following mixing rules are used

$$T_r = \frac{T}{T_c} \qquad\qquad (8\text{-}155)$$

$$P_r = \frac{P}{P_c} \qquad\qquad (8\text{-}156)$$

$$P_c = \frac{R T_c Z_c}{V_c} \qquad\qquad (8\text{-}157)$$

$$V_c = \sum_i x_i V_{c,i} \qquad\qquad (8\text{-}158)$$

$$T_c = \sum_i x_i T_{c,i} \qquad\qquad (8\text{-}159)$$

$$Z_c = \sum_i x_i Z_{c,i} \tag{8-160}$$

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

$$\frac{1}{\lambda_{l,m}^2} = \sum_i \frac{x_i}{\lambda_{l,i}} \tag{8-161}$$

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. 52 and Ref. 53). The pressure dependence is introduced using Equation 8-153 through Equation 8-160. 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. 53) uses an ideal and excess contribution

$$\lambda_{l,m} = \lambda_{l,\text{ideal}} + \lambda_{l,\text{excess}} \tag{8-162}$$

The ideal part is based on mass fractions

$$\lambda_{l,\text{ideal}} = \sum_i \omega_i \lambda_{i,l} \tag{8-163}$$

$$\omega_i = \frac{x_i M_i}{\sum_j x_j M_j} \tag{8-164}$$

The excess term is based on NRTL local concentrations

$$\lambda_{l, \text{excess}} = \frac{\displaystyle\sum_i \sum_j \varpi_i \varpi_j G_{j,i} (\lambda_{j,i} - \lambda_{i,l})}{\displaystyle\sum_j \varpi_j G_{j,i}} \tag{8-165}$$

where $G_{j,i}$ follows from Equation 8-58. The binary interaction terms follow from

$$\lambda_{i,j} = \lambda_{j,i} = \frac{\overline{\varpi}_i \overline{\varpi}_{i,i} \lambda_{i,l} + \overline{\varpi}_j \overline{\varpi}_{j,j} \lambda_{j,l}}{\overline{\varpi}_i \overline{\varpi}_{i,i} + \overline{\varpi}_j \overline{\varpi}_{j,j}} \tag{8-166}$$

which is symmetric, and on the diagonal,

$$\lambda_{i,i} = \lambda_{i,l} \tag{8-167}$$

and

$$\overline{\varpi}_{i,i} = \overline{\varpi}_i (\overline{\varpi}_i + \overline{\varpi}_j G_{j,i}) \tag{8-168}$$

with $\overline{\varpi}_i$ is the composition in the binary mixture of species i and j and the local composition is equi-molar

$$\overline{\varpi}_i = \frac{M_i \sqrt{G_{j,i}}}{M_i \sqrt{G_{j,i}} + M_j \sqrt{G_{i,j}}} \tag{8-169}$$

All liquid thermal conductivity correlations must be specified. The pressure dependence is introduced using Equation 8-153 – Equation 8-160. 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 8-54 to Equation 8-65.

Local Composition (Modified)

Rowley (Ref. 52) adapted the local composition model by replacing the mixing rule in Equation 8-166 by the following

$$\lambda_{i,j} = \lambda_{j,i} = \frac{M_i (\overline{\varpi}_i \overline{\varpi}_{i,i}) \lambda_{i,l} + M_j (\overline{\varpi}_j \overline{\varpi}_{j,j}) \lambda_{j,l}}{M_i (\overline{\varpi}_i \overline{\varpi}_{i,i}) + M_j (\overline{\varpi}_j \overline{\varpi}_{j,j})} \tag{8-170}$$

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. 34 which is valid in the following range:

$$273.15 \text{ K } \leq T \leq 773.15 \text{ K} \qquad p \leq 100 \text{ MPa} \qquad (8\text{-}171)$$

$$773.15 \text{ K } \leq T \leq 923.15 \text{ K} \qquad p \leq 70 \text{ MPa} \qquad (8\text{-}172)$$

$$923.15 \text{ K } \leq T \leq 1073.15 \text{ K} \qquad p \leq 40 \text{ MPa} \qquad (8\text{-}173)$$

VISCOSITY

Vapor

Wilke

Wilke, see Ref. 35, based his method for mixture viscosity of the vapor phase on kinetic theory:

$$\eta_v = \sum_i \left(\frac{x_i \eta_{i,v}}{\sum_j x_j \Psi_{i,j}} \right) \qquad (8\text{-}174)$$

$$\Psi_{i,j} = \frac{\left(1 + \sqrt{\frac{\eta_{i,v}}{\eta_{j,v}}} \left(\frac{M_j}{Mi}\right)^{1/4}\right)^2}{\sqrt{8\left(1 + \frac{M_i}{M_j}\right)}} \qquad (8\text{-}175)$$

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. 36) uses the same basic equation as Wilke (Equation 8-174). However, Equation 8-175 is replaced by

$$\psi_{i,j} = S_{i,j}A_{i,j}\sqrt{\frac{\eta_{i,v}}{\eta_{j,v}}} \tag{8-176}$$

and the interaction parameter is defined as

$$A_{i,j} = \frac{\beta_{i,j}}{\sqrt{RM_{i,j}}}\left(1 + \frac{RM_{i,j} - RM_{i,j}^{0.45}}{2(1 + RM_{i,j}) + \dfrac{1 + RM_{i,j}^{0.45}}{(\sqrt{\beta_{i,j}})(1 + RM_{i,j})}}\right) \tag{8-177}$$

where

$$\beta_{i,j} = \left(\frac{4M_iM_j}{(M_i + M_j)^2}\right)^{1/4}, \quad RM_{i,j} = \frac{M_i}{M_j} \tag{8-178}$$

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. 37) Stockmayer's polar parameter $\delta_{s,i}$(Ref. 38 and Ref. 39) are specified for both species i and j then

$$S_{i,j} = \frac{1 + \sqrt{\dfrac{T^2}{\varepsilon_i\varepsilon_j}} + \dfrac{1}{4}\delta_{s,i}\delta_{s,j}}{\sqrt{1 + \dfrac{T}{\varepsilon_i} + \dfrac{1}{4}\delta_{s,i}}\sqrt{1 + \dfrac{T}{\varepsilon_j} + \dfrac{1}{4}\delta_{s,j}}} \tag{8-179}$$

Otherwise,

$$S_{i,j} = 1 \tag{8-180}$$

Davidson

The Davidson method, see Ref. 40, requires fewer compound specific parameters than Brokaw, while reported accuracy is almost as good, and in the case of H_2, even surpasses it. The Davidson model only requires molar masses and the viscosities of the pure gases. The model is based on fluidity, which is defined to be the reciprocal viscosity.

$$f = \frac{1}{\eta} \tag{8-181}$$

The fluidity of the mixture is then calculated as

$$f = \sum_{i,j} \left(\frac{y_i y_j}{\sqrt{\mu_i}\sqrt{\mu_j}} \cdot E_{i,j}^A \right) \tag{8-182}$$

where y_i is the momentum fraction of species i; $E_{i,j}$ is the momentum transfer coefficient of the species pair i, j; and A is an empirical species-independent parameter set to $1/3$. The momentum fraction is given by

$$y_i = \frac{x_i \sqrt{M_i}}{\sum_j (x_j \sqrt{M_j})} \tag{8-183}$$

and the momentum transfer coefficient is taken as

$$E_{i,j} = \frac{2 \sqrt{M_i}\sqrt{M_j}}{M_i + M_j} \tag{8-184}$$

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:

$$\Delta\eta_{v,P} = \left(\frac{\sqrt{M_t}P_c^{2/3}}{T_c^{1/6}} \right) \left(\frac{10^{-7}}{101325^{2/3}} \zeta \right) \tag{8-185}$$

where ξ is calculated from the correlation of Jossi (Ref. 41), 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:

$$(\xi + 1)^{\frac{1}{4}} = 1.0230 + 0.23364\rho_r + 0.58533\ \rho_r^2 \tag{8-186}$$

$$- 0.40758\ \rho_r^3 + 0.093324\ \rho_r^4$$

$$\rho_r = \frac{\rho}{\rho_c} \tag{8-187}$$

$$\rho_c = \frac{1}{V_c} \tag{8-188}$$

The following mixture rules are used

$$P_c = \frac{RT_c Z_c}{V_c}, \; V_c = \sum_i x_i V_{c,i}, \; T_c = \sum_i x_i T_{c,i} \tag{8-189}$$

$$Z_c = \sum_i x_i Z_{c,i}, \; M_t = \sum_i x_i M_i \tag{8-190}$$

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, Brokaw, and Davidson mixture models. The vapor viscosity follows from

$$\eta_v = \eta_{v,\text{Wilke}} + \Delta\eta_{v,P} \tag{8-191}$$

where $\eta_{v,\text{Wilke}}$ is calculated from Equation 8-174.

Pedersen Corresponding States Model

The corresponding states viscosity model of Pedersen (Ref. 42 and Ref. 43) 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. 44, modified by Pedersen and Fredenslund (Ref. 45) to avoid issues below 91 K where CH_4 becomes solid

$$\eta_{CH_4} = \eta_{CH_4, 0} + \rho_{CH_4}\eta_{CH_4, 1} + F_1\eta_{CH_4, 2} + F_2\eta_{CH_4, 3} \tag{8-192}$$

where

$$F_1 = \frac{H+1}{2} \tag{8-193}$$

$$F_1 = \frac{1-H}{2} \tag{8-194}$$

$$H = \frac{\exp(\Delta T) - \exp(-\Delta T)}{\exp((\Delta T) + \exp(-\Delta T))} \tag{8-195}$$

$$\Delta T = T - 91 \text{ K} \qquad (T \in K) \tag{8-196}$$

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

$$\eta_{CH_4, 0} = \frac{-L_1}{T} + \frac{L_2}{T^{2/3}} - \frac{L_3}{T^{1/3}}$$

$$+ L_4 - L_5 T^{1/3} + L_6 T^{2/3} - L_7 T + L_8 T^{4/3} - L_9 T^{5/3}$$

(8-197)

The first density correction for the moderately dense gas is given by

$$\eta_{CH_4, 1} = L_{10} - L_{11}\left(1.4 - \ln\frac{T}{168\ K}\right)^2$$

(8-198)

The remainder is given by the empirical correlation

$$\eta_{CH_4, 2} = \exp\left(\frac{L_{12}}{T} - L_{13}\right)\left(\exp\left[\left(\sqrt[10]{\rho_{CH_4}}\right)\left(L_{14} - \frac{L_{15}}{T^{3/2}}\right) + \right.\right.$$

(8-199)

$$\left.\left.\left(\frac{\rho_{CH_4} - \rho_{c, CH_4}}{\rho_{c, CH_4}}\right)\left(\sqrt{\rho_{CH_4}}\right)\left(L_{16} + \frac{L_{17}}{T} + \frac{L_{18}}{T^2}\right)\right] - 1\right)$$

The correction term for solid CH_4

$$\eta_{CH_4, 3} = \exp\left(\frac{L_{19}}{T} - L_{20}\right)\left(\exp\left[\left(\sqrt[10]{\rho_{CH_4}}\right)\left(L_{21} - \frac{L_{22}}{T^{3/2}}\right)\right.\right.$$

(8-200)

$$\left.\left. + \left(\frac{\rho_{CH_4} - \rho_{c, CH_4}}{\rho_{c, CH_4}}\right)\left(\sqrt{\rho_{CH_4}}\right)\left(L_{23} + \frac{L_{24}}{T} + \frac{L_{25}}{T^2}\right)\right] - 1\right)$$

with the values of the parameters L_1 through L_{25} are listed in Table 8-5 below:

TABLE 8-5: 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

TABLE 8-5: METHANE VISCOSITY NUMERICAL COEFFICIENTS.

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. 46) is solved for the density of CH_4

$$P = N_1 \rho_{CH_4} T + \rho_{CH_4}^2 \left(-N_2 T + N_3 \sqrt{T} - N_4 + \frac{N_5}{T} - \frac{N_6}{T^2} \right) \tag{8-201}$$

$$+ \rho_{CH_4}^3 \left(N_7 T - N_8 + \frac{N_9}{T} - \frac{N_{10}}{T^2} \right) + \rho_{CH_4}^4 \left(-N_{11} T + N_{12} + \frac{-N_{13}}{T} \right) + N_{14} \rho_{CH_4}^5$$

$$+ \rho_{CH_4}^6 \left(-\frac{N_{15}}{T} + \frac{N_{16}}{T^2} \right) + N_{17} \frac{\rho_{CH_4}^7}{T} + \rho_{CH_4}^8 \left(\frac{N_{18}}{T} + \frac{N_{19}}{T^2} \right) + N_{20} \frac{\rho_{CH_4}^9}{T}$$

$$+ \exp(-N_{21} \rho_{CH_4}^2) \left(\rho_{CH_4}^3 \left(\frac{N_{22}}{T^2} - \frac{N_{23}}{T^3} \right) + \rho_{CH_4}^5 \left(\frac{N_{24}}{T^2} + \frac{N_{25}}{T^4} \right) + \rho_{CH_4}^7 \left(\frac{N_{26}}{T^2} + \frac{N_{27}}{T^3} \right) \right.$$

$$\left. + \rho_{CH_4}^9 \left(-\frac{N_{28}}{T^2} - \frac{N_{29}}{T^4} \right) + \rho_{CH_4}^{11} \left(-\frac{N_{30}}{T^2} + \frac{N_{31}}{T^3} \right) + \rho_{CH_4}^{13} \left(\frac{N_{32}}{T^2} - \frac{N_{33}}{T^3} + N_{34} T^4 \right) \right)$$

where ρ_{CH4} is used in mol/l.

TABLE 8-6: COEFFICIENTS IN THE FUNCTIONAL FORM OF THE MCCARTY EOS.

N_1	0.08205616	N_{13}	2.8685285973	N_{25}	$1.6428375992 \cdot 10^6$
N_2	0.018439486666	N_{14}	$0.11906973942 \cdot 10^{-3}$	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}	$0.1185701681 \cdot 10^{-4}$
N_5	848.44027562	N_{17}	$0.24986828379 \cdot 10^{-4}$	N_{29}	31.630780767
N_6	42738.409106	N_{18}	$0.57974531455 \cdot 10^{-5}$	N_{30}	$0.4100678294 \cdot 10^{-5}$
N_7	$0.76565285254 \cdot 10^{-3}$	N_{19}	0.0071648329297	N_{31}	0.0014870043284
N_8	0.48360724197	N_{20}	$0.12577853784 \cdot 10^{-3}$	N_{32}	$3.151226153 \cdot 10^{-9}$
N_9	85.195473835	N_{21}	0.0096	N_{33}	$0.2167077474 \cdot 10^{-5}$
N_{10}	16607.434721	N_{22}	22240.102466	N_{34}	$0.2400055107 \cdot 10^{-4}$
N_{11}	$0.37521074532 \cdot 10^{-4}$	N_{23}	$1.4800512328 \cdot 10^6$		
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

$$\eta_m = \left(\frac{T_c}{T_{c,\,CH_4}}\right)^{\frac{-1}{6}}\left(\frac{P_c}{P_{c,\,CH_4}}\right)^{2/3}\left(\frac{M_m}{M_{CH_4}}\right)^{1/2}\left(\frac{\alpha}{\alpha_{CH_4}}\right)\eta_{CH_4,\,P_0,\,T_0} \qquad (8\text{-}202)$$

where the CH_4 viscosity $\rho_{CH4,P0,T0}$ is calculated at temperature T_0 and pressure P_0:

$$T_0 = \left(\frac{T_{c,\,CH_4}}{Tc}\right)T\left(\frac{\alpha_{CH_4}}{\alpha}\right) \qquad (8\text{-}203)$$

$$P_0 = \left(\frac{P_{c,\,CH_4}}{Pc}\right)P\left(\frac{\alpha_{CH_4}}{\alpha}\right) \qquad (8\text{-}204)$$

The following mixing rules are used for the critical properties, see Ref. 47:

$$T_c = \frac{\displaystyle\sum_i\sum_j x_i x_j \beta_{i,j}\sqrt{T_{c,i}T_{c,j}}}{\displaystyle\sum_i\sum_j x_i x_j \beta_{i,j}} \qquad (8\text{-}205)$$

$$P_c = \frac{8\displaystyle\sum_i\sum_j x_i x_j \beta_{i,j}\sqrt{T_{c,i}T_{c,j}}}{\left(\displaystyle\sum_i\sum_j x_i x_j \beta_{i,j}\right)^2} \qquad (8\text{-}206)$$

$$\beta_{i,j} = \left(\left(\frac{T_{c,i}}{P_{c,i}}\right)^{1/3} + \left(\frac{T_{c,j}}{P_{c,j}}\right)^{1/3}\right)^3 \qquad (8\text{-}207)$$

The parameter α is

$$\alpha = 1 + 7.378\times10^{-3}\rho_r^{1.847}M_m^{0.5173} \qquad (8\text{-}208)$$

$$\rho_r = \frac{\rho_{CH_4,\,P_0,\,T_0}}{\rho_{c,\,CH_4}} \qquad (8\text{-}209)$$

where

$$T_0 = \left(\frac{T_{c,\,CH_4}}{Tc}\right)T \qquad (8\text{-}210)$$

$$P_0 = \left(\frac{P_{c,\,CH_4}}{Pc}\right)P \tag{8-211}$$

with $\rho_{c,CH4} = 0.16284$ g/cm^3. For CH$_4$

$$\alpha_{CH_4} = 1 + 7.378\times10^{-3}\rho_r^{1.847}M_{CH_4}^{0.5173} \tag{8-212}$$

where Equation 8-209 is used. The mixture molecular weight is a function of the weight-averaged molecular weight and the number-averaged molecular weight

$$M_m = 1.304\times10^{-4}(M_W^{2.303} - M_N^{2.303}) + M_N \tag{8-213}$$

$$M_W = \frac{\displaystyle\sum_i x_i M_i^2}{M_N} \tag{8-214}$$

$$M_N = \sum_i x_i M_i \tag{8-215}$$

where the power in Equation 8-213 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. 48–Ref. 49 for industrial application which is valid in the following range:

$$273.16 \text{ K} \leq T \leq 1173.15 \text{ K} \qquad 0 \leq p \leq p_t \tag{8-216}$$

$$T_m(p) \leq T \leq 1173.15 \text{ K} \qquad p_t \leq p \leq 300 \text{ MPa} \tag{8-217}$$

$$T_m(p) \leq T \leq 873.15 \text{ K} \qquad 300 \text{ MPa} \leq p \leq 350 \text{ MPa} \tag{8-218}$$

$$T_m(p) \leq T \leq 433.15 \text{ K} \qquad 350 \text{ MPa} \leq p \leq 500 \text{ MPa} \tag{8-219}$$

$$T_m(p) \leq T \leq 373.15 \text{ K} \qquad 500 \text{ MPa} \leq p \leq 1000 \text{ MPa} \tag{8-220}$$

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

$$\ln \eta_{l,m} = \sum_i x_i \ln \eta_{i,l} \tag{8-221}$$

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

$$\ln \eta_{l,m} = \sum_i \omega_i \ln \eta_{i,l} \tag{8-222}$$

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

$$\eta_{l,m} = \left(\sum_i x_i \eta_{i,l}^{1/3} \right)^3 \tag{8-223}$$

The model is noted in Ref. 50 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

$$\eta_{l,m} = \left(\sum_i \omega_i \eta_{i,l}^{1/3} \right)^3 \qquad (8\text{-}224)$$

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. 48–Ref. 49 for industrial application which is valid in the following range:

$$273.16\text{K} \le T \le 1173.15\text{K} \qquad 0 \le p \le p_t \qquad (8\text{-}225)$$

$$T_m(p) \le T \le 1173.15 \text{ K} \qquad p_t \le p \le 300 \text{ MPa} \qquad (8\text{-}226)$$

$$T_m(p) \le T \le 873.15 \text{ K} \qquad 300 \text{ MPa} \le p \le 350 \text{ MPa} \qquad (8\text{-}227)$$

$$T_m(p) \le T \le 433.15 \text{ K} \qquad 350 \text{ MPa} \le p \le 500 \text{ MPa} \qquad (8\text{-}228)$$

$$T_m(p) \le T \le 373.15 \text{ K} \qquad 500 \text{ MPa} \le p \le 1000 \text{ MPa} \qquad (8\text{-}229)$$

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 $D_{i,j}$, represents the inverse drag coefficient of species i moving past species j (Ref. 54–Ref. 57). This

property is referred to as the Maxwell–Stefan diffusivity. The Maxwell–Stefan diffusivity is symmetric, $D_{i,j} = D_{j,i}$, and the diagonal elements $D_{i,i}$ are not used.

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 and others (Ref. 58) 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:

$$D_{i,j}^0 = \frac{1.01325 \times 10^{-2} T^{1.75} \sqrt{\frac{1}{M_i} + \frac{1}{M_j}}}{P \left(\left(\sum_i v \right)^{\frac{1}{3}} + \left(\sum_j v \right)^{\frac{1}{3}} \right)^2} \qquad (8\text{-}230)$$

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. 59):

TABLE 8-7: 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

TABLE 8-7: ATOMIC AND STRUCTURAL DIFFUSION VOLUME INCREMENTS.

GROUP	CONTRIBUTION
I	29.8
S	22.9
Aromatic Ring	-18.3
Heterocyclic Ring	-18.3

For some simple molecules the values below, determined from regression, are used:

TABLE 8-8: 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. 60) also modified the Chapman–Enskog relation to correlate binary diffusion coefficient in vapor phase according to:

$$D_{i,j}^0 = 10^{-2} \times \frac{\left(3.03 - \left(\dfrac{0.98}{\sqrt{MW_{i,j}}}\right)\right) T^{1.5}}{P\sigma_{i,j}^2 \Omega_D \sqrt{MW_{i,j}}} \tag{8-231}$$

where

$$MW_{i,j} = \frac{2}{\dfrac{1}{M_i} + \dfrac{1}{M_j}} \tag{8-232}$$

The length scale $\sigma_{i,j}$ for the interaction is taken from the Lennard–Jones diameter parameters of species i and j:

$$\sigma_{i,j} = \frac{(\sigma_i^{LJ} + \sigma_j^{LJ})}{2} \tag{8-233}$$

If σ_i^{LJ} is not specified in the database, it is instead estimated from:

$$\sigma_i^{LJ} = 1.18 \times 10^{-8} V_{i,l,b}^{\frac{1}{3}} \tag{8-234}$$

where $V_{i,l,b}$ is the molar volume of species at normal boiling point.

The collision integral Ω_D is evaluated from (Ref. 61):

$$\Omega_D = 1.06036\, T^{*-0.15610} + 0.19300\, \exp\,(\text{-}0.47635\, T^*) \tag{8-235}$$
$$+\, 1.03587\, \exp\,(\text{-}1.52996\, T^*) + 1.76474\, \exp\,(\text{-}3.89411\, T^*)$$

with

$$T^* = \frac{T}{\varepsilon_{i,j}} \tag{8-236}$$

The energy scale $\varepsilon_{i,j}$ for the interaction is taken from the Lennard–Jones energy parameters of species i and j:

$$\varepsilon_{i,j} = \sqrt{\varepsilon_i^{LJ} \varepsilon_j^{LJ}} \tag{8-237}$$

If ε_i^{LJ} is not specified in the database, it is instead estimated from:

$$\frac{\varepsilon_i^{LJ}}{k} = 1.15\, T_{i,l,b} \tag{8-238}$$

where k is the Boltzmann constant and $T_{i,l,b}$ is the 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

$$D_{i,j} = D_{i,j}^0 \qquad (i \neq j) \qquad (8\text{-}239)$$

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, $V_{i,l,b}$ 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, $V_{i,l,b}$ 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, $V_{i,l,b}$ 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 other 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. 62) for liquid phase diffusion coefficients at infinite dilution is:

$$D_{i,j}^0 = 1.858795959 \times 10^{-18} \frac{T \sqrt{\phi_j M_j}}{\eta_j V_{i,l,b}^{0.6}} \tag{8-240}$$

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 8-9: ASSOCIATION PARAMETERS FOR SOLVENT.

SOLVENT	ASSOCIATION PARAMETER
Water	2.26 (Ref. 63)
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. 64) is applied where liquid molar volume of water at normal boiling point, $V_{\text{water},l,b}$ is multiplied by 4.5.

Tyn–Calus

The Correlation by Tyn and Calus (Ref. 65) for liquid diffusion coefficients at infinite dilution reads:

$$D_{i,j}^0 = 8.93 \times 10^{-16} \frac{T\left(V_{i,l,b}^{\frac{1}{6}}\right)P_j^{0.6}}{\eta_j\left(V_{j,l,b}^{\frac{1}{3}}\right)P_i^{0.6}} \tag{8-241}$$

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 or 1-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. 66) 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:

$$D_{i,j}^0 = 1.25 \times 10^{-12} T^{1.52} \left(\frac{0.07244359601}{V_{i,l,b}^{0.19}} - 0.292 \right) \tag{8-242}$$

$$\times (\eta_j \times 10^3)^{\left(\frac{9.58 \times 10^{-6}}{V_{i,l,b}} - 1.12 \right)}$$

Normal paraffin solutions: In case both the solute and solvent are normal paraffins (derived from SMILES formula), the correlation reads:

$$D_{i,j}^0 = 7.30889362 \times 10^{-16} T^{1.47} \left(\frac{(\eta_j \times 10^3)^{\left(\frac{10.2 \times 10^{-6}}{V_{i,l,b}} - 0.791 \right)}}{V_{i,l,b}^{0.71}} \right) \tag{8-243}$$

For all other systems, the correlation is:

$$D_{i,j}^0 = 3.8934239 \times 10^{-16} \frac{T^{1.29} \sqrt{P_j}}{\eta_j^{0.92} (V_{j,l,b}^{0.23}) P_i^{0.42}} \tag{8-244}$$

If the solvent is nonpolar (dipole moment is zero), and the solvent is methanol, ethanol or 1-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. 67) 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:

$$D_{i,j}^0 = 1.295436901 \times 10^{-17} \frac{T}{\eta_j^{1.026} (V_{i,l,b}^{0.5473})} \tag{8-245}$$

For all other systems, the equation for organic solution is used as:

$$D_{i,j}^0 = 1.459473761 \times 10^{-15} \frac{T(V_{j,l,b}^{0.265})}{\eta_j^{0.907}(V_{i,l,b}^{0.45})} \qquad (8\text{-}246)$$

Where T is the temperature, $V_{i,l,b}$ is the liquid volume at normal boiling point and η_j is the viscosity of the solvent.

Erkey–Rodden–Akgerman

The correlation by Erkey and others (Ref. 68) for liquid diffusion coefficients at infinite dilution in normal paraffins is:

$$D_{i,j}^0 = 94.5 \times 10^{-9} \frac{\sqrt{T}(V - V_j^{ref}) \times 10^6}{M_i^{0.239} M_j^{0.781} (\sigma_i \sigma_j \times 10^{-20})^{1.134}} \qquad (8\text{-}247)$$

where the reference volume is

$$V_j^{ref} = \frac{1}{\sqrt{2}} b_j N_{Av} \sigma_j^3 \qquad (8\text{-}248)$$

N_{Av} is Avogadro's number, and the deviation from closest packing volume is given by

$$b_j = 1.206 + 0.0632 \left(\frac{\sigma_i}{\sigma_j}\right) \qquad (8\text{-}249)$$

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. 69), and for some species are taken from Ref. 68 and Ref. 70 as:

TABLE 8-10: 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 $(V - V_j^{ref})$ 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. 71) model for diffusion in binary solutions can be extended to multicomponent systems (Ref. 72):

$$D_{i,j} = \prod_{k=1}^{n} (D_{i,j,x_k \to 1})^{x_k} \tag{8-250}$$

where $D_{i,j,x_k \to 1}$ 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. 57) becomes unity and the Maxwell–Stefan diffusivity equals to Fick diffusivity:

$$D_{i,j,x_j \to 1} = D_{i,j}^0 = D_{i,j}^0 \tag{8-251}$$

Similarly,

$$D_{i,j,x_i \to 1} = D_{j,i}^0 = D_{j,i}^0 \tag{8-252}$$

Models for the $D_{i,j,x_k \to 1}$ for $k \neq i$ and $k \neq j$ remain to be defined in such a way that symmetry is ensured:

$$D_{i,j} = D_{j,i} \tag{8-253}$$

and to ensure continuity if both species i and j vanish:

$$\lim_{x_i \to 0} D_{i,j,x_k \to 1} = \lim_{x_j \to 0} D_{i,j,x_k \to 1} \tag{8-254}$$

For binary systems, Equation 8-250 reduces to the Vignes interpolation formula.

Wesselingh–Krishna

Wesselingh and Krishna (Ref. 72) proposed:

$$D_{i,j,x_k \to 1} = \sqrt{D_{i,j}^0 D_{j,i}^0} \tag{8-255}$$

leading to:

$$D_{i,j} = (D_{i,j}^0)^{(1 + x_j - x_i)/2}(D_{j,i}^0)^{(1 + x_i - x_j)/2} \tag{8-256}$$

Kooijman–Taylor

Kooijman and Taylor (Ref. 73) found on a limited number of systems that this provides better results:

$$D_{i,j,\,x_k \to 1} = \sqrt{D_{i,k}^0 D_{j,k}^0} \qquad (k \neq i, j) \tag{8-257}$$

leading to:

$$D_{i,j} = (D_{i,j}^0)^{x_j}(D_{j,i}^0)^{x_i} \prod_{\substack{k\,=\,1 \\ k \neq i,j}}^{n} (\sqrt{D_{i,k}^0 D_{j,k}^0})^{x_k} \tag{8-258}$$

Wesselingh and Bollen (Ref. 74) asserted that this is a reasonable estimate.

Krishna–van Baten

Krishna and van Baten (Ref. 75), on the basis of data obtained from molecular dynamic simulations, proposed the following Vignes-based (Ref. 71) interpolation:

$$D_{i,j,\,x_k \to 1} = (D_{i,k}^0)^{\left(\frac{x_i}{x_i + x_j}\right)}(D_{j,k}^0)^{\left(\frac{x_j}{x_i + x_j}\right)} \qquad (k \neq i, j) \tag{8-259}$$

The model reduces to the Kooijman–Taylor model for $x_i = x_j$. The value of $D_{i,j,\,x_k \to 1}$ 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 $D_{i,j,\,x_k \to 1}$ itself, the equation is modified to:

$$D_{i,j,\,x_k \to 1} = (D_{i,k}^0)^{\left(\frac{x_i + \varepsilon_x}{x_i + x_j + 2\varepsilon_x}\right)}(D_{j,k}^0)^{\left(\frac{x_j + \varepsilon_x}{x_i + x_j + 2\varepsilon_x}\right)} \qquad (k \neq i, j) \tag{8-260}$$

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:

$$D_{i,j} = (D_{i,j}^0)^{x_j}(D_{j,i}^0)^{x_i} \prod_{\substack{k=1 \\ k \neq i,j}}^{n} \left((D_{i,k}^0)^{\left(\frac{x_i + \varepsilon_x}{x_i + x_j + 2\varepsilon_x}\right)} (D_{j,k}^0)^{\left(\frac{x_j + \varepsilon_x}{x_i + x_j + 2\varepsilon_x}\right)} \right)^{x_k} \tag{8-261}$$

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.

$$\sigma_{vl} = \sum_i x_{i,l} \sigma_{i,vl} \tag{8-262}$$

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. 76), the vapor-liquid surface tension is predicted by mixing the pure species correlations according to

$$\sigma_{vl} = \frac{\displaystyle\sum_i \sum_j \frac{x_{i,l} x_{j,l} \sqrt{\sigma_{i,vl}\sigma_{j,vl}}}{\rho_{i,l}\rho_{j,l}}}{\left(\displaystyle\sum_i \frac{x_{i,l}}{\rho_{i,l}}\right)^2} \tag{8-263}$$

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.

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9

Multiphysics Coupling Nodes

The Fuel Cell & Electrolyzer Module has multiphysics couplings available under certain conditions.

When a predefined multiphysics interface is added from the **Model Wizard** or **Add Physics** windows, it adds the constituent interfaces and the **Multiphysics Couplings** node, which automatically includes one or more multiphysics couplings.

If the constituent physics interfaces are added one at a time, then it adds an empty **Multiphysics Couplings** node. When you right-click this node, you can choose from the available multiphysics couplings.

Q   The Multiphysics Branch in the *COMSOL Multiphysics Reference Manual*.

In this chapter, the following multiphysics couplings nodes are described:

- Electrochemical Heating
- Potential Coupling

- Space Charge Density Coupling
- Reacting Flow, H2/O2 Gas Phase

Electrochemical Heating

Use the **Electrochemical Heating** multiphysics coupling ( ) to define domain and boundary heat sources in a heat transfer interface, based on the sum of irreversible (Joule heating and activation losses) and reversible heat in an electrochemistry interface. The node also defines the temperature in the electrochemistry interface to be equal to that of the heat transfer interface.

The settings of this node are similar to the Electromagnetic Heating node, described in the *COMSOL Multiphysics Reference Manual*.

> 🔍   Theory for Electrochemical Heat Sources

Potential Coupling

The **Potential Coupling** multiphysics coupling ( ) applies the electrolyte potential variable from the source interface into the model inputs of the destination interface. The potential variable is typically used to compute the migration flux in the destination interface.

COUPLED INTERFACES

Specify the physics interface that provides the potential (Electrostatics, for instance) in the **Source** list and the Chemical Species Transport interface in the **Destination** list.

Space Charge Density Coupling

The **Space Charge Density Coupling** multiphysics coupling ( ) computes the local space charge, based on the local concentrations and species charges in a Chemical Species Transport interface, and adds it to Poisson's equation in an Electrostatics interface.

COUPLED INTERFACES

Specify the Chemical Species Transport interface in the **Source** list and the Electrostatics interface in the **Destination** list.

Reacting Flow, H2/O2 Gas Phase

The **Reacting Flow, H2 Gas Phase** and the **Reacting Flow, O2 Gas Phase** nodes couple a fluid flow interface to a **Hydrogen Fuel Cell** (fc) or a **Water Electrolyzer** (we) interface.

The node sets up a two-way bidirectional coupling so that the velocity field and pressure distribution, calculated by the fluid flow interface, are used by the fc/we interface, whereas the density and dynamic viscosity, calculated by the fc/we interface, are used by the fluid flow interface.

10

Glossary

This Glossary of Terms contains application-specific terms used in the Fuel Cell & Electrolyzer 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

anode An electrode where oxidation occurs. Anodic charge transfer current densities and overpotentials are positive by definition.

cathode An electrode where reduction occurs. Cathodic charge transfer current densities and overpotentials are negative by definition.

cell voltage The difference in potential over an electrochemical cell.

charge transfer reaction A reaction during which charge is transferred from an electron conducting phase (electrode) to an ion conducting phase (electrolyte).

charge transfer current density The current density at an electrolyte-electrode interface associated with a charge transfer reaction.

concentrated electrolyte An electrolyte where the concentration of charged species is so high that the interactions (friction forces) between the ions needs to be considered. See also diluted electrolyte.

current collector A part of an electrochemical device with high electric conductivity for conducting current out of the cell. See also current feeder.

current feeder A part of an electrochemical device with high electric conductivity for conducting current into the cell. See also current collector.

diluted electrolyte An electrolyte where the charged species are diluted in a solvent so that the interaction between the ions can be neglected. See also concentrated electrolyte.

electric potential The potential in the electrode (electron conducting) phase, denoted ϕ_s (phis).

electrode An electron conductor.

electrode reaction See charge transfer reaction.

electrokinetic flow Transport of fluid or charged particles within a fluid by means of electric fields.

electrolyte An ion conductor.

electrolyte potential The potential in the electrolyte (ionic) phase, denoted ϕ_l (phil).

electroneutrality A situation where the net charge of any small control volume of a domain is zero. Electroneutrality can usually be assumed for electrolytes, with an exception for the very proximity of the electrolyte-electrode interface, which is due to the charge separation within the electrochemical double layer.

equilibrium potential The potential difference between the electrode and electrolyte at which the net current density of an electrode reaction is zero.

Faraday's Law A mathematical expression relating the flux of a species over an electrode-electrolyte interphase to be proportional to the charge transfer current density.

gas diffusion electrode (GDE) A porous electrode that also includes gas pores in the porous matrix.

gas diffusion layer (GDL) A porous matrix containing an electron conducting media and gas pores. A gas diffusion layer contains no electrolyte phase.

GDL See gas diffusion layer (GDL).

GDE See gas diffusion electrode (GDE).

Gibbs free energy A thermodynamic potential that depends on the enthalpy and entropy of the reacting species.

intrinsic volume averages The physical properties of the fluid, such as density, viscosity, and pressure.

intercalation The process of ions reacting on the surface of a host particle to form a solid, intercalated, species within the host. The intercalated species can then be transported further into the particle by diffusion processes.

migration The transport of charged species in an electrolyte due to the electric force imposed by the electric field.

morphology correction parameter A correction parameter that is used to account for morphology effects of a porous structure.

Nernst–Planck equation A commonly used equation for describing the transport of charged species in a diluted electrolyte. The equation includes transport due to diffusion, migration and convection. The Nernst–Planck equation can be modeled in COMSOL Multiphysics using the Tertiary Current Distribution, Nernst–Planck interface (and the Transport of Diluted Species interface). The Nernst–Planck equation is often combined with an electroneutrality condition.

Nernst–Planck–Poisson equation In certain situations, for instance when striving to resolve the electrochemical double layer at an electrode, and electroneutrality cannot be assumed, the Nernst–Planck equation is combined with the Poisson's equation for describing the charge density.

overpotential A deviation from the equilibrium potential.

oxidation A charge transfer reaction where electrons are produced.

perfectly mixed electrolyte. An electrolyte where no concentration gradients are present, for instance due to stirring. See also secondary current distribution.

primary current distribution The current distribution that is established when overpotentials can be neglected — that is, when the current distribution is governed by the electrolyte and electrode conductivities only. See also secondary current distribution and tertiary current distribution.

Poisson's equation An equation for relating the electric field to the space charge density. Can be modeled in COMSOL using the Electrostatics interface.

pore electrolyte An electrolyte in the pores of a porous matrix. See porous electrode.

porous electrode A porous matrix containing both electron conducting and ion conducting media.

potentiostat A device that monitors and controls the potential of an electrode versus a reference electrode.

reduction A charge transfer reaction where electrons are consumed.

reference electrode An electrode used for reference when defining the potentials of the electrodes in a cell. A good reference electrode is stable and does not vary in

potential. Typically no net reactions occur at a reference electrode surface, and the net current density is zero.

resistive film A film with ohmic resistivity, typically formed as a result of electrode reactions.

secondary current distribution The current distribution that is established when concentration overpotentials can be neglected — that is, when the current distribution is governed by the activation overpotentials and the electrolyte conductivity. See also tertiary current distribution and primary current distribution. Note that COMSOL models using the Secondary Current Distribution interface can in fact be modeling a tertiary current distribution because mass transport activation losses can be present in the electrode reaction current density expressions.

solid-electrolyte interphase (SEI) A resistive and passivating layer formed on the graphite electrode particles in the negative electrode of a lithium-ion battery.

stoichiometric coefficients The number of species reacting in a reaction formula. In a redox reaction the oxidized species have negative sign and the reduced species have positive sign by convention.

superficial volume averages The flow velocities, which correspond to a unit volume of the medium including both pores and matrix. These are sometimes called Darcy velocities, defined as volume flow rates per unit cross section of the medium.

supporting electrolyte An electrolyte with an excess of charge carriers so that the conductivity can be assumed not to be affected by the currents flowing in the cell.

surface molar flux The tangential flux in the surface dimension as governed by diffusion according to Fick's law.

tertiary current distribution The current distribution that is established when concentration overpotentials cannot be neglected — that is, when the current distribution is governed by the activation and concentration overpotentials, as well as the electrolyte conductivity. The electrolyte conductivity can also be nonconstant due to the currents flowing in the cell. See also secondary current distribution and primary current distribution.

Index