Corrosion Module

User's Guide

COMSOL

Corrosion Module User's Guide

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Introduction

This guide describes the Corrosion Module, an optional add-on package for COMSOL Multiphysics® intended for the modeling and simulation of corrosion and corrosion protection processes.

This chapter introduces you to the capabilities of this 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.

In this chapter:

• About the Corrosion Module
• Overview of the User's Guide

About the Corrosion Module

These topics are included in this section:

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

The Physics Interfaces and Building a COMSOL Multiphysics Model in the *COMSOL Multiphysics Reference Manual*

What Can the Corrosion Module Do?

The Corrosion Module is intended for the modeling of corrosion and corrosion protection. The descriptions made available by the module are based on current and potential distribution in galvanic cells. Its modeling capabilities cover galvanic corrosion, cathodic protection, anodic protection, and sacrificial anode protection.

The Corrosion Module consists of chemical species transport, fluid flow, heat transfer, electrochemistry, and corrosion interfaces. These physics interfaces describe the potential in the electrolyte and in the corroding or protected metallic structure. The electrode reactions can be described using arbitrary electrode kinetic expressions of the overpotential for the anodic and cathodic reactions. The potential and current distribution can also include the influence of mass transport and heat transfer, which means that the Corrosion Module makes it possible to model composition and temperature in a corrosion cell in detail. The ability to account for mass transport in the electrolyte allows for modeling of corrosion caused by variations in, for example, salt concentration, oxygen concentration, and pH.

The basis of the Corrosion Module is the mass and current balances in the electrolyte and in the corroding or protected metal structure. In the electrolyte, the current balance is defined together with individual species balances for the charged species and the electroneutrality condition. In the metallic structure, the current balance is described using Ohm's law for the current density. The electron transfer reactions, at the interface between the metallic structure and the electrolyte, couple the transport processes in the electrolyte with the current flowing in the metallic structure. The

module contains predefined formulations for the abovementioned processes. In addition, the module can be used together with the heat transfer interfaces using predefined terms for heat sources caused by the electrochemical process.

Corrosion Module Physics Interface Guide

The Corrosion Module extends the functionality of the physics interfaces of the base package for COMSOL Multiphysics. The details of the physics interfaces and study types for the Corrosion Module are listed in the table. The functionality of the COMSOL Multiphysics base package is listed in the *COMSOL Multiphysics Reference Manual*.

	In the *COMSOL Multiphysics Reference Manual:*
	• Studies and Solvers
Q	• The Physics Interfaces
	• For a list of all the core physics interfaces included with a COMSOL Multiphysics license, see Physics Interface Guide.

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
⋮⋮ Chemical Species Transport				
Surface Reactions		sr	all dimensions	stationary (3D, 2D, and 2D axisymmetric models only); time dependent
Transport of Diluted Species		tds	all dimensions	stationary; time dependent
Transport of Diluted Species in Porous Media		tds	all dimensions	stationary; time dependent
Transport of Diluted Species in Fractures		dsf	3D, 2D, 2D axisymmetric	stationary; time dependent
Electrophoretic Transport		el	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
Chemistry		chem	all dimensions	stationary; time dependent
Nernst-Planck-Poisson Equations		tds+es	all dimensions	stationary; time dependent; stationary source sweep; small-signal analysis, frequency domain
Reacting Flow				
Laminar Flow, Diluted Species		—	3D, 2D, 2D axisymmetric	stationary; time dependent
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
Current Distribution, Boundary Element		cdbem	3D, 2D	stationary; stationary with initialization; time dependent; time dependent with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
Current Distribution, Shell		cdsh	3D, 2D, 2D axisymmetric	stationary; stationary with initialization; time dependent; time dependent with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent
Current Distribution, Pipe		cdpipe	3D	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
Corrosion, Deformed Geometry				
Corrosion, Primary		cd + dg	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent
Corrosion, Secondary				

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
Corrosion, Tertiary with (Electroneutrality, Supporting Electrolyte)		tcd + dg	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent
≋ Fluid Flow				
🌐 Porous Media and Subsurface Flow				
Brinkman Equations		br	3D, 2D, 2D axisymmetric	stationary; time dependent
Darcy's Law		dl	all dimensions	stationary; time dependent
Free and Porous Media Flow		fp	3D, 2D, 2D axisymmetric	stationary; time dependent
⸨ Heat Transfer				
Heat Transfer in Porous Media		ht	all dimensions	stationary; time dependent
▌ Moving Interface				
Level Set		ls	all dimensions	time dependent with phase initialization

Common Physics Interface and Feature Settings and Nodes

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

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

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

Where Do I Access the Documentation and Application Libraries?

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

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

THE DOCUMENTATION AND ONLINE HELP

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

Opening Topic-Based Help
The Help window is useful as it is connected to the features in the COMSOL Desktop. To learn more about a node in the Model Builder, or a window on the Desktop, click to highlight a node or window, then press F1 to open the Help window, which then

displays information about that feature (or click a node in the Model Builder followed by the **Help** button (?)). This is called *topic-based* (or *context) help*.

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

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

Opening the Documentation Window

Win	To open the **Documentation** window: • Press Ctrl+F1. • From the **File** menu select **Help>Documentation** (▪).

Mac **Linux**	To open the **Documentation** window: • Press Ctrl+F1. • On the main toolbar, click the **Documentation** (▪) button. • From the main menu, select **Help>Documentation**.

THE APPLICATION LIBRARIES WINDOW

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

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

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

Opening the Application Libraries Window
To open the **Application Libraries** window (▥):

Win	• From the **Home** toolbar, **Windows** menu, click (▥) **Applications Libraries**. • From the **File** menu select **Application Libraries**. To include the latest versions of model examples, from the **File>Help** menu, select (▥) **Update COMSOL Application Library**.

Mac Linux	Select **Application Libraries** from the main **File>** or **Windows>** menus. To include the latest versions of model examples, from the **Help** menu select (▥) **Update COMSOL Application Library**.

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Events	www.comsol.com/events
COMSOL Video Gallery	www.comsol.com/video
Support Knowledge Base	www.comsol.com/support/knowledgebase

Overview of the User's Guide

The *Corrosion 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 ELECTROCHEMISTRY BRANCH

Corrosion, Deformed Geometry Interfaces chapter describes the Corrosion, Primary and the Corrosion, Secondary and the Corrosion, Tertiary Nernst-Planck interfaces and the underlying theory for electrode deformations.

Electrochemistry Interfaces chapter describes the Primary Current Distribution, Secondary Current Distribution, Tertiary Current Distribution, Nernst-Planck, Current Distribution on Edges, BEM, Electrode, Shell, and Electroanalysis interfaces. The chapter also includes the underlying theory.

THE CHEMICAL SPECIES TRANSPORT BRANCH

Chemical Species Transport Interfaces chapter describes the Transport of Diluted Species, Transport of Diluted Species in Porous Media and the Surface Reactions interfaces. It also includes sections about the underlying theory for each physics interface.

THE FLUID FLOW BRANCH

Fluid Flow Interfaces chapter describes the Brinkman Equations, Darcy's Law, and Free and Porous Media Flow interfaces and underlying theory.

THE HEAT TRANSFER BRANCH

Heat Transfer Interfaces chapter describes how to couple electrochemical heat sources to heat transfer.

THE MULTIPHYSICS COUPLING NODES

The Multiphysics Coupling Nodes chapter describes the coupling nodes available under the Multiphysics node for coupling various electrochemical interfaces using potential or space charge density couplings, for example.

2

Modeling with Electrochemistry

In this chapter you are given an 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 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, in designing a battery, for example, 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 electrolyte. 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 current 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 electrolyte. 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.

ℚ	• Potential Variables
	• Current Variables and Calculating the Total Cell Current

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 the cases of more advanced nonlinear charge conservation equations being required and concentration-dependent electrode polarization, 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.
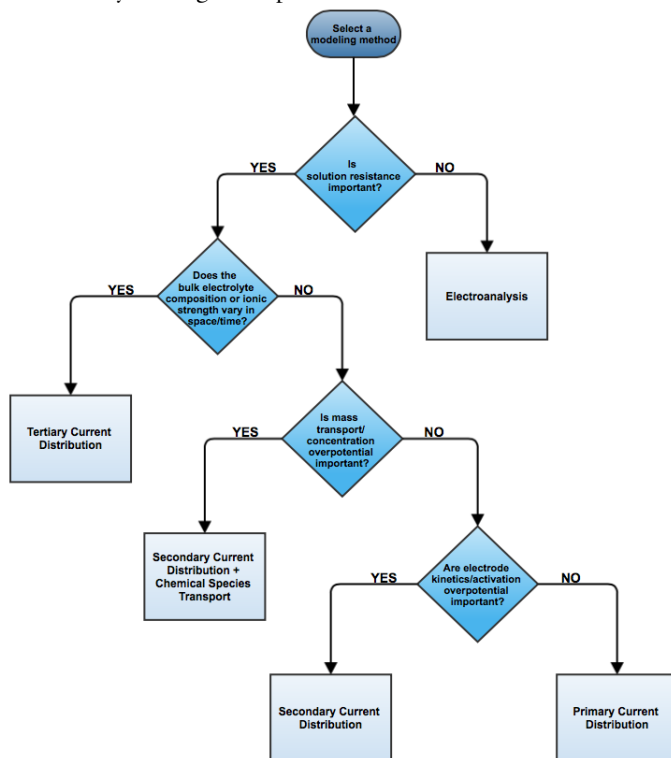
Understanding the Different Approximations for Conservation of Charge in Electrolytes

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**, but they are highly nonlinear and difficult to converge. Most often, further approximations can simplify the problem without compromising accuracy.

Q
- 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.

Q
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 right-most 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:

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

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 $\mathbf{E} = 0$. 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:

$$Ag^+(aq) + e^- \leftrightarrow Ag(s)$$
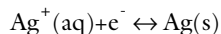
This reaction is called a "half-cell" reaction, since it will occur at a specific electrode-electrolyte interface. It cannot occur in isolation, but only when coupled to another half-cell reaction within a two-electrode electrochemical cell. Each reaction has a characteristic Gibbs energy change that 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

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

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 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 expression 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 need to be set up manually by the Electrode Surface Coupling nodes. When modeling porous electrodes, the corresponding coupling node to create a source/sink 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, the number of electrons transferred per mole of reactant, in a reductive direction and F the Faraday constant (96485 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:

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

In this formulation the exchange current density, i_0, is defined as:

$$i_0 = i_{0,0} c_R^{\alpha_c/n} c_O^{\alpha_a/n} \tag{2-6}$$

where $i_{0,0}$ is the exchange current density at standard conditions.

The overpotential is here defined as

$$\eta = E - E_{eq} \tag{2-7}$$

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

$$E_{eq} = E_{eq,0} - \frac{RT}{nF}\ln\frac{c_R}{c_O} \tag{2-8}$$

and $E_{eq,0}$ is the equilibrium potential at standard conditions.

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 $c_O \rightarrow 0$ or $c_R \rightarrow 0$), the factor $\ln\frac{c_R}{c_O}$ may get 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 $c_{R,ref}$ and $c_{O,ref}$ (typically corresponding to the inlet or initial concentrations), resulting in

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

where

$$i_{0,ref} = i_{0,0} c_{R,ref}^{\alpha_c/n} c_{O,ref}^{\alpha_a/n} \tag{2-10}$$

and

$$\eta = E - E_{eq,ref} \tag{2-11}$$

with

$$E_{eq,ref} = E_{eq,0} - \frac{RT}{nF} \ln \frac{c_{R,\,ref}}{c_{O,\,ref}} \qquad (2\text{-}12)$$

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 (*non-faradaic 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 non-faradaic 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.

Common Simplifications When Modeling Electrochemical Cells

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 an 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.

?	• Electrochemistry Interfaces
	• Specifying Initial Values and Meshing Techniques in the *COMSOL Multiphysics Reference Manual*

ELECTROCHEMISTRY COUPLED TO MASS TRANSPORT

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.)

	• Electrochemistry Interfaces
	In the *COMSOL Multiphysics Reference Manual:*
ℚ	• 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:*
ℚ	• Step and Time Dependent
	• Building a COMSOL Multiphysics Model and The Events Interface

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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.

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

🔍	Studies and Solvers and Building a COMSOL Multiphysics Model in the *COMSOL Multiphysics Reference Manual*

POTENTIAL VARIABLES

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

TABLE 2-1: 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

TABLE 2-2: COMMON CURRENT DENSITY VARIABLES.

VARIABLE	UNIT	DESCRIPTION	DEFINED AT
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.IlMag	A/m^2	Electrolyte current density magnitude (L^2 norm)	Electrolyte domains
xxx.IsMag	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

Electrochemistry Interfaces

This chapter describes the generic physics interfaces to model electrochemical cells. The physics interfaces described are found under the **Electrochemistry** branch ( ).

In this chapter:

- Shared Physics Features in the Electrochemistry Interfaces
- The Primary and Secondary Current Distribution Interfaces
- The Current Distribution, Boundary Elements Interface
- The Current Distribution, Shell Interface
- The Current Distribution, Pipe Interface
- The Tertiary Current Distribution, Nernst-Planck Interface
- The Electrode, Shell Interface
- The Electroanalysis Model Wizard Entry
- Theory for the Current Distribution Interfaces
- Theory for Electrochemical Heat Sources
- Theory for the Electrode, Shell Interface

- Theory for Electroanalysis
- Electrode Potentials and Reference Electrodes

Shared Physics Features in the Electrochemistry Interfaces

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

Electrochemistry Interfaces interfaces have these domain, 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).

Most 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.

- Double Layer Capacitance
- Circuit Terminal
- Electric Ground
- Electric Potential
- Electric Reference Potential
- Electrode
- Electrode Current
- Electrode Current Density
- Electrode Current Source
- Electrode-Electrolyte Boundary Interface
- Electrode Potential
- Electrode Reaction
- Electrode Surface
- Electrode Reaction
- Electrode Current
- Electrolyte Current Density

- Electrolyte Current Source
- Electrolyte Potential
- External Short
- Harmonic Perturbation
- Initial Values for Dissolving-Depositing Species
- Insulation
- Internal Electrode Surface
- Line Mass Source[1]
- Non-Faradaic Reactions
- Point Mass Source[1]
- Porous Electrode Reaction
- 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

Electrode

Use the **Electrode** 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.

---

⑦	Electrode Theory

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 non-faradaic 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: $1/\text{m}$).

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

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.

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** (▤) buttons as needed in the tables 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. The growth rate can be used in conjunction with the Deforming Electrode Surface and Nondeforming Boundary multiphysics couplings to model geometry deformations.

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 an 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.

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
💡	Use The Surface Reactions Interface to model surface diffusion.

SPECIES CONSERVATION ON DEFORMING GEOMETRY

In Deforming Geometry simulations, the Compensate for Boundary Stretching adds a tangential convection term, based on the movement of the mesh, to the mass balance equations of the dissolving-depositing species surface concentrations.

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: $\Omega \cdot m^2$) 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.

BOUNDARY 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:
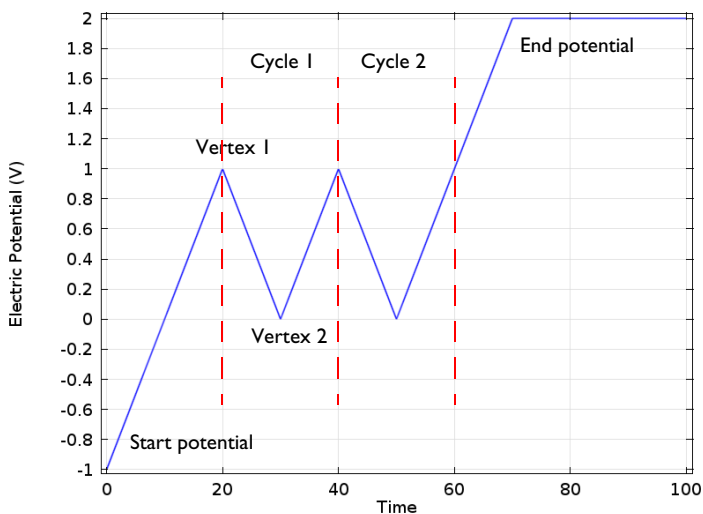
Figure 3-1: Electric potential vs time generated by the cyclic voltammogram boundary condition. The linear sweep rate is 100 mV/s, the number of cycles is 2. Potentials levels are also shown.

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 **Smoothing of cyclic voltammetry wave functions** check box is selected by default and the **Smoothing factor**

defaults to $1\cdot10^{-3}$. When enabled, smoothing is applied on the triangular wave around the vertex potentials. The smoothing zone corresponds to the product of the smoothing factor with half the duration of one period of the triangular wave.

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.

| ℚ | • 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** $E_{\text{eq, ref}}$ (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 $E_{\text{eq}}=E_{\text{eq, ref}}$).

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 $E_{\text{eq}}=E_{\text{eq, ref}}$.

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.

For all 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).

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** $i_{0,ref}$ (A/m^2), which is the exchange current density when $E_{eq}=E_{eq, ref}$.

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 pre-exponential 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

and 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:

$$\sum_{\text{ox}} v_{\text{ox}} S_{\text{ox}} + n e^- \Leftrightarrow \sum_{\text{red}} v_{\text{red}} S_{\text{red}} \tag{3-1}$$
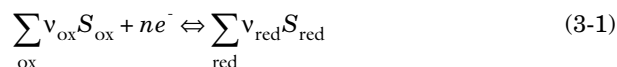
Set v_i as positive (v_{red}) for the reduced species and negative (v_{ox}) for the oxidized species in an electrochemical reaction. The number of participating electrons, n, should be positive.

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 non-faradaic 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 a 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.

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.
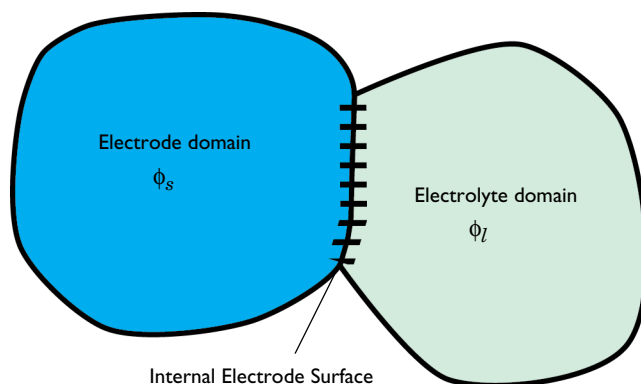
The node can only be applied at interior boundaries between electrode and electrolyte domains. Note that, due to the high conductivity of many electrode materials, an Electrode domain can many times be replaced an external condition at the electrolyte boundary. For such cases, consider using the Electrode Surface instead.

For a description of the Film Resistance, Dissolving-Depositing Speciesand Constraint Settings sections, see the Electrode Surface node.

- Electrode Reactions Theory

Thin Electrode Surface

Use the **Thin Electrode Surface** node to define electrode reactions occurring on a thin electrode, fully immersed in electrolyte. The electrode is assumed to be infinitely thin, and is only applicable to interior boundaries of electrolyte domains.

The node can be used as an alternative to drawing the actual electrode domain in the model geometry, and may significantly reduce meshing and solver time, especially in 3D models. The node can typically be used to model electrodeposition or corrosion processes occurring on thin sheets of metal.

The functionality of the node is similar to the Electrode Surface node. Use the **Side selection** setting to define if the electrode reactions, defined by the Electrode Reaction subnodes, are to be defined **Both** sides of the electrode, or on the **Up** or **Down** side only.

Upon application of the node, the electrolyte potential dependent variable degree of freedom is defined as a "slit" with different values on each side on the selected boundaries. Additional variables defined by the node depending on the electrolyte potential, also having different values on each side of the internal boundary, are named using additional u or d postfixes, indicating to which (up or down) side they apply.

> Q The up and down operators in the *COMSOL Multiphysics Reference Manual*

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,** $\phi_{l, \text{bnd}}$ (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.

🔍	Thin Insulating Layer Theory

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 a 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. It is also available and described here for the Corrosion, Deformed Geometry 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.

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.

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.

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.

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.

🔍	Frequency Domain Perturbation Study Step in the *COMSOL Multiphysics Reference Manual*

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.

🔍	Electrode Potentials and Reference Electrodes

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, $\phi_{s,\,\text{here}}$, and the integrated current over the boundary will be computed according to Ohm's law:

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

$$\phi_{s,\,\text{here}} \colon \int_{d\Omega} (\mathbf{n} \cdot \mathbf{I}_s) \mathrm{d}d\Omega = -\frac{\phi_{s,\,\text{here}} - \phi_{s,\,\text{there}}}{R}$$

where $\phi_{s,\,\text{there}}$ (V) is the potential of the connected electrode. Use the **Connected Potential** list to choose among available connection potentials for the value of $\phi_{s,\,\text{there}}$.

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.

Non-Faradaic Reactions

Use the **Non-Faradaic Reactions** node to define the reaction rate for dissolving-depositing species due to non-faradaic (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.

See Electrode Reaction for information about the settings of this section.

Q	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.

Q	Electrode Potentials and Reference Electrodes

Circuit Terminal

This feature is only available with an AC/DC Module or a Batteries & Fuel Cells Module license.

Use the **Circuit Terminal** node to specify a coupling to the **External I vs U** node in the **Electrical Circuit** interface.

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
- Infinite Electrolyte
- 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
- Sacrificial Edge Anode

> 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 Electrochemistry Interfaces

The Primary Current Distribution and Secondary Current Distribution Interfaces

The **Primary Current Distribution (cd)** interface ( ) and the **Secondary Current Distribution (cd)** interface ( ) are both 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 with the difference that it 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.

Ohm's law is used in combination with a charge balance to describe the conduction of currents in the electrodes and electrolytes.

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.

Q   • 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.

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.

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 from this list also 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.

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.

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 Electrochemistry Interfaces • Theory for the Current Distribution Interfaces

⊞	• Primary Current Distribution: *Corrosion Protection of an Oil Platform Using Sacrificial Anodes* Application Library path **Corrosion_Module/Cathodic_Protection/oil_platform**. • Secondary Current Distribution: *Galvanized Nail*: Application Library path **Corrosion_Module/Galvanic_Corrosion/galvanized_nail**

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.

🔍	• Domain Equations for Primary and Secondary Current Distributions • Electrolyte Theory

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.

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, the gas diffusion layer (GDL) in a PEMFC electrode — 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.

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

Infinite Electrolyte

The **Infinite Electrolyte** defines an electrolyte of infinite extension.

The node can only be applied to external boundaries that are adjacent to an Electrolyte domain. The infinite electrolyte is located outside these boundaries.

The **Infinity condition** defines the condition for the electrolyte potential at infinity.

Note that the **Electrolyte conductivity** σ_l (SI unit: S/m) entered cannot be space dependent.

The node solves for the Laplace equation using the boundary element method (BEM). It is available in 2D and 3D.

When enabled, the **Symmetry Lines** (2D) or **Symmetry Planes**(3D) defines an even symmetry (insulation) line/plane with infinite extension at the specified position. Boundaries coinciding with **Symmetry Lines** or **Symmetry Planes** should not be included in the Boundary Selection.

𝄚	*Corrosion Protection of a Ship Hull*: Application Library path **Corrosion_Module/Cathodic_Protection/ship_hull**

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.

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.

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.

DISSOLVING-DEPOSITING SPECIES

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

Use the **Add** (➕) and **Delete** (▤) buttons as needed in the tables to control the number of species.

Dependent variables for the molar concentration (SI unit: mol/m) are added for each dissolving-depositing species. These variables can be used to keep track of the amount of reacted material on the electrode. The total molar dissolution/deposition rate depends on the reaction rates and stoichiometry, defined in the **Electrode Reaction** sub nodes.

The **Density** and **Molar mass** determine the electrode growth velocity and the resulting dissolved/deposited layer thickness, so that the change in the edge electrode radius also can be calculated. By use of the **Add volume change to edge radius** check box you may define if this volume change should be included in the model.

A thickness variables is also defined that you for instance can use to couple to the Film Resistance (see below).

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** $q_{l,s}$ (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** $q_{l,l}$ (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** $q_{l,s}$ (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.

Sacrificial Edge Anode

Use the **Sacrificial Edge Anode** node to model rod-shaped dissolving metal electrodes in corrosion protection applications. The node is defined on an edge in a 3D geometry, and the electrochemical reactions are defined on a virtual tube in the geometry, located at a given radius around the edge. A Sacrificial Edge Anode can only be applied to

edges within, or adjacent to, Electrolyte domains. The node is only available when a **Secondary** Current distribution type has been chosen on the top node.

As the metal electrode dissolves, the edge radius decreases. In time-dependent simulations, the node solves for a capacity (SI unit: C/m) degree of freedom to keep track of the total amount of passed charge along the edge. The edge radius is defined so that it equals **Initial radius** (m) at the **Initial capacity** (SI unit: C/m)**,** reaching the **Terminal radius** (m) when the capacity reaches zero.

The actual dissolution rate is defined by the Electrode Reaction subnodes. By enabling **Set current density to zero at depletion**, all current densities are set to zero when the capacity goes to zero, using a smoothed step function. The **Size of transition zone** value sets the relative capacity for which the smoothing starts close to depletion.

Enable **Add tangential diffusion** to improve convergence by smoothing out local capacity gradients along the edges.

The potential in the electronic phase is used by the Electrode Reaction subnodes in the kinetics expressions. It can be defined by a **Fixed** electric potential, a **Floating potential** or an **External short** electric potential. The floating potential allows to specify the total current flowing through all edges selected by the node. The External short allows to connect two electrodes over an external connector with a given bulk resistance.

FILM RESISTANCE
See the Electrode Surface 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 **Initial radius** in order to achieve good numerical accuracy.

Wiring Edges

Use this node to define multiple, separate, connected anodes, defined by the same **Sacrificial Edge Anode** node.

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

The edge capacity dependent variable at the **Sacrificial Edge Anode** node is not solved for along the edge selection of this node.

The Current Distribution, Boundary Elements Interface

The **Current Distribution, Boundary Elements (cdbem)** interface (▢), found under the **Electrochemistry** branch (▮▯) when adding a physics interface, solves for the electrolyte potential using the Laplace equation. The equations are formulated and solved for by the use of the Boundary Element Method (BEM). The interface is available for 2D and 3D components.

Due to the use of BEM, current source terms in the electrolyte, and porous electrodes, cannot be used in this interface.

The individual node settings of the **Current Distribution, Boundary Elements** are in most cases identical to the corresponding nodes in The Primary and Secondary Current Distribution Interfaces. This chapter will only cover features and settings specific for the **Current Distribution, Boundary Elements** interface.

The Current Distribution, Boundary Elements Interface

SETTINGS

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

DOMAIN SELECTION

The interface supports selection of voids.

When the **Infinite void** is selected the boundary element formulation includes infinity. Use the settings of the Infinity Condition section to set the boundary condition for the potential at infinity.

Note: The default domain selection of the interface is All domains and voids which includes the Infinite void. The domain number of the infinite void is 0. Another way to add the Infinite void to the selection is to click **Paste Selection** and type in 0.

SYMMETRY

Symmetry can be a convenient way to add insulating boundaries of infinite extension, for instance to model the surface of the ocean in a sub-sea corrosion protection problem.

Use the applicable combo boxes to activate a symmetry plane in 3D space dimension and a symmetry line in 2D space dimension and specify the location (x, y, z) of the plane/line using the **Plane position/Line position** parameter.

FAR FIELD APPROXIMATION

The BEM problem is solved with **Use far field approximation** check box enabled and using an iterative solver by default. The far field approximation in combination with an iterative solver may in many cases lead to a significantly lower computational load.

INFINITY CONDITION

Use the settings of this section to apply a boundary condition for the electrolyte potential at infinity.

The settings are only active if the **Infinite Void** is included in the selection.

QUADRATURE

In this section you can specify the integration orders for different types of elements in the model. A higher integration order increases the accuracy of the computed results but can take longer to compute.

All the integration orders should be at least equal to the discretization order of the dependent variable, but for all but distant elements, higher orders are recommended. The integration order for **Integration order, weak contribution** should be at least twice the discretization order of the dependent variable.

The automatic selection sets the integration orders of all types of elements depending upon the dependent variable discretization order selected in the Discretization section. There is also Manual selection option where the integration orders of all types of elements can be edited.

DISCRETIZATION

In this section you can specify the discretization orders of the dependent variable and of auxiliary boundary element method boundary flux variables.

Note: The discretization order of auxiliary boundary element method edge flux variables is the same as that of the dependent variable.

Edge Features in 3D for the Current Distribution, Boundary Elements Interface.

The edge nodes in the interface contain some extra settings compared to the edge nodes in The Primary and Secondary Current Distribution Interfaces

When using edge nodes (in 3D) the interface creates virtual tubes around the edge selections, defined by the **Edge radius** (m).

It is generally assumed that the edge radius is small in comparison to other geometrical measures of the model such as the edge length and the distance between different edges in the geometry. This usually also implies that the decrease of available electrolyte volume for charge transport, due to the space occupied by the tubes, can be neglected. Enable **Compensate for tube volume** to include the effect of the volume of the tubes on the electrolyte charge transfer.

Note that additional degrees of freedoms are introduced in the model when compensating for the tube volume, and that this may result in higher memory usage and longer solver times.

@	• The Primary and Secondary Current Distribution Interfaces • Shared Physics Features in the Electrochemistry Interfaces • Theory for the Current Distribution Interfaces

▦	*Corrosion Protection of Multiple Oil Platforms*: Application Library path **Corrosion_Module/Cathodic_Protection/multiple_oil_platforms**.

The Current Distribution, Shell Interface

The **Current Distribution, Shell (cdsh)** interface (![icon]), found under the **Electrochemistry** branch (![icon]) when adding a physics interface, describes the electrolyte charge transport in thin electrolyte layers in the tangential direction on a boundary. By replacing the domain electrolyte partial differential equation by a tangential formulation on the boundary, the problem size can be reduced, and potential problems with mesh anisotropy in the thin layer can be avoided.

The physics interface is typically used for atmospheric corrosion problems, but is suitable for any problem with thin electrolytes layers where the potential variation in the normal direction to the boundary is negligible.

The interface is similar to The Primary and Secondary Current Distribution Interfaces, but solves for the electrolyte potential (phil) only, on the boundaries to the geometry. The interface is available in 2D, 2D with axial symmetry, and 3D.

Feature Nodes in the Current Distribution, Shell Interface

Compared to The Primary and Secondary Current Distribution Interfaces, the following differences should be noted:

• The thickness of the thin electrolyte layer is specified on the Electrolyte node.

• The Electrode Surface node has the same dimension as the Electrolyte node. That is, the thin Electrolyte is assumed to be located on top of the Electrode Surface.

	Atmospheric Corrosion of a Busbar: Application Library path **Corrosion_Module/Galvanic_Corrosion/atmospheric_corrosion_busbar**.

The Current Distribution, Pipe Interface

The **Current Distribution, Pipel (cdpipe)** interface ( ), found under the **Electrochemistry** branch ( ) when adding a physics interface, describes the electrolyte charge transport in electrolyte tubes of a given radius along the tangential direction of an edge.

By replacing the domain electrolyte partial differential equation by a tangential formulation along the edge, the problem size can be significantly reduced.

The physics interface is typically used for corrosion and corrosion protection simulations inside metallic pipes.

The interface is similar to The Primary and Secondary Current Distribution Interfaces, but solves for the electrolyte potential (phil) only, on the edges in the geometry. The interface is only available in 3D.

Feature Nodes in the Current Distribution, Pipe Interface

Compared to The Primary and Secondary Current Distribution Interfaces, the following differences should be noted:

• The radius of the pipes is specified on the Electrolyte node and the electrolyte ionic conduction is assumed to occur within the tubular volume defined by the radius and the edge.

Pipe Electrode Surface

This node defines the metallic surface located at the inner wall of the tubes, facing the electrolyte.

Regarding the settings of this node, see the Electrode Surface node.

Pipe Point Electrode Surface

This node defines a small electrode located inside the tube, for instance a small area lacking a protective coating. The node is defined in a point, with the area defined by the **Electrode Area** setting.

Regarding the remaining settings of this node, see the Electrode Surface node.

Pipe Point Sacrificial Anode

The node is available on points. The node defines a sacrificial anode, coupled to the pipe over a resistor.

A current source will be inserted in each selected point, depending on the local potential in the electrolyte, the **Anode Equilibrium Potential** and the **Coupled potential**, and the **Coupling resistance**.

The current source will be strictly anodic if **Set current to zero for cathodic potentials** is checked.

CAPACITY

The settings of this section are only applicable for time-dependent simulations.

In time-dependent simulations, the node solves for a capacity (SI unit: C) degree of freedom in each selected point to keep track of the amount of charge inserted into the pipe. The **Initial Capacity** sets the initial value of the capacity (charge) in each selected point.

By enabling **Set current density to zero at depletion**, the current in a point is set to zero when the corresponding capacity in that point reaches zero, using a smoothed step function. The **Size of transition zone value** sets the relative capacity for which the smoothing starts close to depletion.

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

📄	All other nodes in the Tertiary Current Distribution, Nernst-Planck interface are described in Shared Physics Features in the Electrochemistry 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.

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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.

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.

DEPENDENT VARIABLES

This physics interface defines these dependent variables (fields), the **Concentration**s 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: $\mathrm{mol/m}^4$). 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.

Crevice Corrosion of Iron in an Acetic Acid/Sodium Acetate Solution: Application Library path
Corrosion_Module/Crevice_Corrosion/crevice_corrosion_fe

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 coefficient**s (SI unit: m^2/s) 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.

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.

DISSOLVING-DEPOSITING SPECIES

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

See the Electrode Surface node.

Q
- Porous Electrode Theory
- Porous Electrode Reactions Theory
- Domain Equations for Tertiary Current Distributions Using the Nernst-Planck Equations and Electroneutrality

---

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.

Reactions

Use the **Reactions** node to define non-electrochemical 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 will calculate the potential shift over the boundary based on the membrane charge carrying species concentration, or **User defined**.

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

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
- Corroding Electrode
- 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.

Corroding Electrode

The **Corroding Electrode** node implements Equation 3-7 (with no source term), Equation 3-8, and Equation 3-9. Use this node to define the seed layer thickness, the electrode thickness change, the electrical conductivity, and the electrode current density.

The electrode thickness change and electrode current density are typically coupled to an Electrochemistry interface that describes the current distribution in the adjacent domain and the electrode reactions.

CORRODING ELECTRODE

The **Seed layer thickness** s_0 (SI unit: m) defaults to $1 \cdot 10^{-4}$ m.

Enter a value or expression for the **Electrode thickness change** Δs (SI unit: m). The default is 0 m.

The default **Electrical conductivity** σ (SI unit: S/m) uses the value **From material**. For **User defined** select **Isotropic**, **Diagonal**, **Symmetric**, or **Full** depending on the properties of the pore electrolyte. Then enter any expression for the conductivity as a function of temperature. Then enter a value or expression in the field or matrix.

ELECTRODE CURRENT DENSITY

Enter a value or expression for the **Electrode current density** i_n (SI unit: A/m^2). The default is 0 A/m^2.

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** $\mathbf{i}_e$ (SI unit: A/m^2). The defaults are 0 A/m^2.

Current Source

The **Current Source** node adds a source term to Equation 3-7. 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 $\phi_s = 0$.

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.

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 concentration(s).

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.

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

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_i 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.

$$\mathbf{J}_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_l \qquad (3\text{-}2)$$

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 porous electrode theory 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:

$$i_{loc,m} = i_0\left(\exp\left(\frac{\alpha_a F\eta}{RT}\right) - \exp\left(\frac{-\alpha_c F\eta}{RT}\right)\right)$$

where $i_{loc,m}$ denotes the local charge transfer current density for reaction m, i_0 the exchange current density, α_a the anodic transfer coefficient, α_c 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 the species i in the electrolyte is given by the continuity equation, with a flux given by the Nernst-Planck equation:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (\mathbf{J}_i + c_i \mathbf{u}) = R_{i,\text{tot}}$$

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 3-2)

The current balance includes the sum of the flux of all charged species, which yields the current density in the electrolyte:

$$\mathbf{i}_l = F\sum_{i=1}^{n} z_i(-D_i \nabla c_i - z_i u_{\text{m},i} F c_i \nabla \phi_l) = F\sum_{i=1}^{n} z_i \mathbf{J}_i$$

> 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.)

In the equations above, $\mathbf{i}_l$ denotes the current density vector in the electrolyte. The current balance in the electrolyte 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). The current balance and the material balances give one equation per unknown species concentration. However, there is still one more unknown, the *electrolyte potential*, which requires an additional equation. 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:

$$\sum z_i c_i \ = \ 0$$

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 non-Faradaic 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:
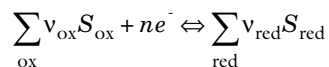
$$\sum_{ox} v_{ox} S_{ox} + ne^- \Leftrightarrow \sum_{red} v_{red} S_{red}$$

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:

$$N_i \ = \ \sum_m \frac{v_{i,m} i_m}{n_m F}$$

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 the *Faraday constant*.

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:

$$R_{i,\,\mathrm{molar}} = -\sum_m a_{v,\,m} \frac{v_{i,\,m} i_m}{n_m F}$$

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 stochiometry, $v_{i,m}$, and the local current density, $i_{\mathrm{loc},m}$, as described in Mass Fluxes and Sources Due to Electrochemical Reactions.

If the reaction rate is known, the total growth $v_{\mathrm{dep,\,tot}}$ (m/s) is defined as the sum of the velocity contributions for all species and electrode reactions according to:

$$v_{\mathrm{dep,\,tot}} = \sum_i \frac{M_i}{\rho_i} \sum_m \frac{v_{i,\,m} i_{\mathrm{loc},\,m}}{n_m F} \qquad (3\text{-}3)$$

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:

$$\frac{\partial \mathbf{x}}{\partial t} \cdot \mathbf{n} = v_{\mathrm{dep,\,tot}}$$

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:

$$2e^- (\text{electrical circuit}) + A^+ (\text{solution}) + X^- (\text{double layer})$$
$$\Rightarrow$$
$$2e^- (\text{electrode surface}) + A^+ (\text{double layer}) + X^- (\text{solution})$$
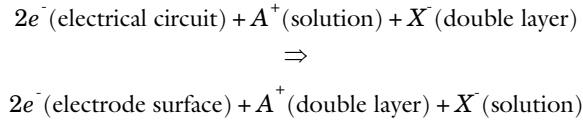
This corresponds to a negative charge of $2F$ being moved from double layer to solution. Following the convention that the reaction is written in the order of cathodic current (as above), then with respect to the free solution species, the cation is a reactant (negative stoichiometry) and the anion is 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:

$$\eta_m = \phi_s - \Delta\phi_{s,\,film} - \phi_l - E_{0,\,m}$$

If the thickness and conductivity of the film are known, the resistance can be written as:

$$R_{film} = \frac{s_0 + \Delta s}{\sigma_{film}}$$

where s_0 is the reference/initial film thickness, Δs the electrode thickness change, and σ_{film} the conductivity (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

$$\sum_{i:\nu_i < 0} |\nu_i| S_i + ne^- \leftrightarrow \sum_{i:\nu_i > 0} |\nu_i| S_i$$
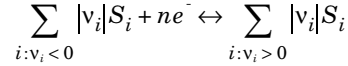
where ν_i is the stoichiometric coefficient of the reacting species of index i and n is the number of participating electrons.

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 $E_{\text{eq, ref}}$ (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 $a_{i, \text{ ref}}$ (unitless).

For ideal conditions, 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 $i_{\text{loc},m}$ are available. In the following 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 (or *reduction potential*). For an electrode reaction, the activation overpotential, denoted η (V), is the following:

$$\eta = \phi_s - \phi_l - E_{\text{eq}}$$

where E_{eq} denotes the equilibrium potential.

THE BUTLER-VOLMER EQUATION

A common kinetics expression in electrochemical modeling is the Butler-Volmer equation:

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

where α_c (unitless) denotes the cathodic charge transfer coefficient, α_a (unitless) the anodic charge transfer coefficient, and i_0 (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 outer-sphere 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 also a concentration dependent equilibrium potential defined by the Nernst equation (see previous section Equilibrium Potentials and the Nernst Equation), and the kinetics to

follow the ideal law of mass action, and the condition that $\alpha_a + \alpha_c = n$, the exchange current density becomes

$$i_0 = i_{0,\text{ref}} \sum_{i:\nu_i > 0} \left(\frac{a_i}{a_{i,\text{ref}}}\right)^{\frac{\alpha_c \nu_i}{n}} \sum_{i:\nu_i < 0} \left(\frac{a_i}{a_{i,\text{ref}}}\right)^{\frac{-\alpha_a \nu_i}{n}}$$

where $i_{0,\text{ref}}$ is the exchange current density (A/m^2) at the reference state. The above expression was derived by observing that, due to the law of mass action, we should also be able to write local current density expression as

$$i_{\text{loc}} = i_{0,\text{ref}} \left(\sum_{i:\nu_i > 0} \left(\frac{a_i}{a_{i,\text{ref}}}\right)^{\nu_i} \exp\left(\frac{\alpha_a F \eta_{\text{ref}}}{RT}\right) - \sum_{i:\nu_i < 0} \left(\frac{a_i}{a_{i,\text{ref}}}\right)^{-\nu_i} \exp\left(\frac{-\alpha_c F \eta_{ref}}{RT}\right) \right)$$

where the reference overpotential η_{ref} (V) is defined as

$$\eta_{\text{ref}} = \phi_s - \phi_l - E_{\text{eq, ref}}.$$

This latter form of the Butler-Volmer equation is preferable from a numerical point of view since it eliminates evaluating the exponentials of two logarithms.

The law of mass action is however not generally valid for complex reactions involving multiple electron steps. For certain multi-electron reactions, where one electron transfer step is rate limiting, is however still possible to derive a lumped Butler-Volmer type of expression using the following expression for the exchange current density (See: Modern Electrochemistry by John O'M. Bockris, Amulka K.N Reddy, and Maria Gamboa-Aldeco. Volume 2A, Second Edition, Chapter 7, Section 7.6. 2000 Kluwer Academic/Plenum Press, New York.):

$$i_0 = i_{0,\text{ref}} \sum_i \left(\frac{a_i}{a_{i,\text{ref}}}\right)^{\gamma_i}$$

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 relates 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 $i_{0,\,\text{ref}} = k_0 F c_{\text{ref}}$, the mass action law expression above can be rewritten as

$$i_{\text{loc}} = k_0 F \left(c_r \exp\left(\frac{\alpha_a F \eta}{RT}\right) - c_o \exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right)$$

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:

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

Here C_R and C_O are dimensionless expressions, describing the dependence on the reduced and oxidized species in the reaction. Note that if $C_O \neq C_R$ when $\eta = 0$, this kinetics expression results in $i_{\text{loc}} \neq 0$, 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:

$$i_{loc} = i_0 \cdot 10^{\eta / A_a}$$

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:

$$i_{loc} = -i_0 \cdot 10^{\eta / A_c}$$

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:

$$i_{\text{loc}} = \frac{i_{\text{expr}}}{1 + \left\| \frac{i_{\text{expr}}}{i_{\text{lim}}} \right\|}$$

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 an cathodic term in the Butler-Volmer equation may be neglected.

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.

⚲
- For the Primary and Secondary Current Distribution interfaces, see Electrolyte.
- For the Tertiary Current Distribution, Nernst-Planck interface, see Electrolyte.

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:

$$\nabla \cdot \mathbf{i}_l = Q_l \ \text{ and } \ \nabla \cdot \mathbf{i}_s = Q_s$$

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 Porous Electrode.
- For the Tertiary Current Distribution, Nernst-Planck interface, see Porous Electrode.

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 Electrode Reaction 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.

Porous Electrode Reaction

ELECTRODE THEORY

Electron conduction in an Electrode 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.

Q | Electrolyte Current Density

ELECTROLYTE CURRENT THEORY

The Electrode Current 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

The Electrode Current adds one unknown variable, the electric potential, $\phi_{s,\text{bnd}}$, along the boundary. It then adds one additional equation for the total current, which is an integral over the boundary:

$$\int_{\partial\Omega} \mathbf{i}_s \cdot \mathbf{n} ds = I_{n,s}$$

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, $I_{n,s}$.

SYMMETRY THEORY

The Symmetry 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 Electrode Current Density 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:

$$\phi_s = \phi_{s,\text{bnd}} \qquad \text{on } \partial\Omega$$

$$\int_{\partial\Omega} (\phi_{s,\text{bnd}} - \phi_{s,\text{ground}})(\mathbf{i}_s \cdot \mathbf{n})dS = P_{\text{total}}$$

where $\phi_{s,\text{ground}}$ is the ground potential of the cell, and P_{total} (W) is the power to be drawn.

For an average power condition, P_{total} is calculated by:

$$P_{\text{total}} = P_{\text{avg}} A$$

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.

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

$$\rho_{\text{fix}} + F\sum z_i c_i = 0$$

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(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 a 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:

$$\mathbf{n} \cdot \mathbf{I}_{l,1} = \mathbf{n} \cdot \mathbf{I}_{l,2}$$

THIN INSULATING LAYER THEORY

The usual approach to adding an insulating body in a model is to add a domain to the geometry and then exclude this domain from the electrolyte. An insulating boundary condition on the boundaries of the insulating body is then used according to

$$\mathbf{n} \cdot \mathbf{I}_l = 0$$

If the model also includes mass transport, no flux conditions are also used for each species on the insulation boundaries.

$$\mathbf{n} \cdot \mathbf{J}_i = 0$$

Introducing very thin domains in the model geometry may however cause issues with meshing and significantly increase the memory requirements during solving because the thin thicknesses of the layers need to be resolved in the mesh.

As an alternative to describing the thin layers as domains in the geometry, the Thin Insulating Layer feature instead models the thin layer as a boundary — that is, a layer of infinitely small thickness — and then mathematically "slits" the dependent variables. The slitting implies that separate degrees of freedoms are used on each side on the boundary. The same boundary conditions as above are then used on each side of the boundary.

Thin Electrode Layer

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 for instance 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

The charge transport in the solid conductor material and electrolyte create joule heating source terms according to

$$Q_{\mathrm{JH}} = -(\mathbf{i}_s \cdot \nabla \phi_s + \mathbf{i}_l \cdot \nabla \phi_l) \tag{3-4}$$

Heating Due to Electrochemical Reactions

For an electrochemical reaction process one can write the total heat balance as:

• Heat generated = Total reaction enthalpy – Electrical energy leaving the system

Using Faraday's law for an electrode reaction, m, at the interface between the electron and ion conducting phase this corresponds to

$$Q_m = \left(\frac{\Delta H_m}{n_m F} - \left(\frac{\Delta G_m}{n_m F} - \eta_{m,\,\mathrm{tot}} \right) \right) i_m \tag{3-5}$$

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 3-5 may now be rearranged into

$$Q_m = \left(\eta_{m,\,\mathrm{tot}} + \frac{T \Delta S_m}{n_m F} \right) i_m \tag{3-6}$$

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 3-5 we have used the total overpotential, $\eta_{m,\mathrm{tot},}$ (including potential effects from film resistances and similar), defined as

$$\eta_{m,\,\mathrm{tot}} = \phi_s - \phi_l - E_{\mathrm{eq},\,m}$$

The equilibrium potential is related to ΔG_m in the following way:

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

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.

Theory for the Electrode, Shell Interface

The Electrode, Shell Interface defines electrode current conduction on 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:

$$\nabla_T \cdot (s\mathbf{i}_s) = -i_n \tag{3-7}$$

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

$$\mathbf{i}_s = -\nabla_T \sigma_s \phi_s \tag{3-8}$$

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

$$s = s_0 + \Delta s_{\text{tot}} \qquad (3\text{-}9)$$

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

$$Q_H = -s\mathbf{i}_s \cdot \nabla_{\text{t}} \phi_s$$

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:

$$\mathbf{N}_i = -D_i\nabla c_i + c_i \mathbf{u} \tag{3-10}$$

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:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{N}_i = R_{i,\text{tot}} \tag{3-11}$$

The Electroanalysis charge conservation model solves Equation 3-10 and Equation 3-11 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:

$$\frac{\partial c_i}{\partial t} = D_i\nabla^2 c_i \tag{3-12}$$

Equation 3-12 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:

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

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:

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

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:

$$N_i = \sum_m \frac{v_{i,m} i_m}{n_m F} \tag{3-13}$$

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:

$$N_i = \mathbf{N}_i \cdot \mathbf{n} \tag{3-14}$$

Equation 3-13 and Equation 3-14 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 non-Faradaic components (i_{nf}) such as current due to Double Layer Capacitance:

$$i_{total} = \sum_m i_{loc, m} + i_{nf}$$

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*:

$$i_{\text{loc}} = k_0 F \left(c_{\text{Red}} \exp\left(\frac{\alpha_a F \eta}{RT}\right) - c_{\text{Ox}} \exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right) \tag{3-15}$$

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 follows $\alpha_a + \alpha_c = 1$.

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:

$$c_{\text{Red}} = c_{\text{Ox}} \exp\left(\frac{-F E_{\text{eq}}}{RT}\right)$$

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 3-15 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:

$$\phi_{s,\,CE}: \qquad \int_{\text{electrodes}} i_{\text{tot}} dS = 0 \qquad\qquad (3\text{-}16)$$

The counter electrode potential is used in the overpotential, η, in the kinetics expression(s) on the counter electrode.

$$\eta_m = \phi_{s,\,CE} - E_{\text{eq},\,m} \qquad\qquad (3\text{-}17)$$

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

$$\eta = \phi_s - \phi_l - E_{eq} \qquad (3\text{-}18)$$

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 3-18 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 a *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:

$$\phi_{s, \text{ref}} = \phi_l + E_{\text{eq, ref}} \qquad (3\text{-}19)$$

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:

$$E_{\text{vs ref}} = \phi_s - \phi_{s, \text{ref}} \qquad (3\text{-}20)$$

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

$$\phi_{s, \text{bnd}} = E_{\text{vs ref}} + \phi_{s, \text{ref}} \qquad (3\text{-}21)$$

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 Reference Electrode 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 3-19. 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 3-20, is also defined in all electrode domains.

The Electric Reference Potential node is a point feature applicable to electrode domains (in all the Electrochemistry interfaces). It defines a global electric reference potential $\phi_{s,\,\text{ref}}$ (SI unit: V) equal to the dependent variable ϕ_s (SI unit: V) in the point. 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.

Whenever a $\phi_{s,\,\text{ref}}$ is defined, the variable $E_{\text{vs ref}}$ (SI unit: V), according to Equation 3-20, is also defined in all electrode domains.

The Electrode Potential 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 3-21. 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 $E_{\text{vs ref}}$ (SI unit: V), according to Equation 3-20, is also defined on these features.

4

Corrosion, Deformed Geometry Interfaces

This chapter describes the physics interface found under the **Electrochemistry>Corrosion, Deformed Geometry** branch ( ).

In this chapter:

• About the Corrosion Interfaces

About the Corrosion Interfaces

The **Corrosion, Primary** ( ), the **Corrosion, Secondary** ( ), and the **Corrosion, Tertiary Nernst-Planck** ( ), found under the **Electrochemistry>Corrosion, Deformed Geometry** branch ( ) in the Add Physics menu, are predefined multiphysics interfaces for time-dependent modeling of deformations that occur as a result of deposition/dissolution processes in electrochemical cells.

Use these physics interfaces to investigate geometrical changes in corrosion cells.

By choosing one of the above multiphysics interfaces, the corresponding **Current Distribution** interface and a **Deformed Geometry** interface are added to the component. **Deforming Electrode Surface** and **Non-Deforming Boundary** multiphysics coupling nodes that couple electrode reactions to boundary velocities are also added by default. The predefined couplings are set up so that the deforming geometry velocity is set to the total depositing velocity on boundaries where deposition/dissolution processes occur, and zero on all other boundaries.

Note that is also possible to extend an already existing current distribution model to include electrode deformations by manually adding a Deformed Geometry interface and the required Multiphysics coupling nodes.

> • The Primary Current Distribution and Secondary Current Distribution Interfaces
> • The Tertiary Current Distribution, Nernst-Planck Interface
> • The Deformed Geometry Interface in the *COMSOL Multiphysics Reference Manual*
> • The Multiphysics Branch in the *COMSOL Multiphysics Reference Manual*
> • Deforming Electrode Surface multiphysics coupling node
> • Nondeforming Boundary multiphysics coupling node

Modeling Deformation of an Electrode Surface

The deposition rate and electrode growth velocity is defined by the Current Distribution interface by the use of an Electrode Surface (applicable to external

boundaries to an Electrolyte domain) or an Internal Electrode Surface (applicable to interior boundaries between an Electrolyte and an Electrode domain).

Use the Dissolving-Depositing species section in the Electrode Surface node to specify what species are participating in the electrode reactions, and use the Electrode Reaction sub nodes to specify the reaction kinetics and stoichiometry.

An arbitrary number of dissolving-depositing species can be added on an electrode surface. The surface concentration variables of the deposited species can be used to calculate the thickness of the deposited layer, and the depositing rate is used to set the boundary velocity for the deforming geometry.

Dissolution/deposition is always assumed to occur in the normal direction to an electrode boundary, with the velocity being directed into the electrolyte domain:

$$\frac{\partial \mathbf{x}}{\partial t} \cdot \mathbf{n} = v_{\text{dep, tot}} \tag{4-1}$$

where $v_{\text{dep, tot}}$ is the total growth velocity, defined as the sum of the velocity contributions for all species and electrode reactions according to:

$$v_{\text{dep, tot}} = \sum_i \frac{M_i}{\rho_i} \sum_m \frac{\nu_{i,m} i_{\text{loc},m}}{n_m F} \tag{4-2}$$

Where M_i (SI unit: kg/mol) is the molar mass and ρ_i (SI unit: kg/m^3) the density of the species.

The boundary condition is implemented similarly to the Normal Mesh Velocity boundary node in the Deformed Geometry interface.

Tangential Velocities at the Intersection Between a Depositing and a Noncorroding Boundary

Shared points (in 2D) or edges (in 3D) between corroding and noncorroding boundaries are handled specifically in the Corrosion, Deformed Geometry interfaces.

The deformation in the normal direction of a noncorroding boundary is set to zero at all times. However, for the deformation velocity of the shared points/boundaries in the tangential direction of the noncorroding boundary, special conditions apply. These conditions can be derived expressions by assuming growth/dissolution to occur only

in the normal direction of the corroding boundary by addition or removal of spherical particles (for example metal atoms), see Figure 4-1 below.

Noncorroding material

Noncorroding material
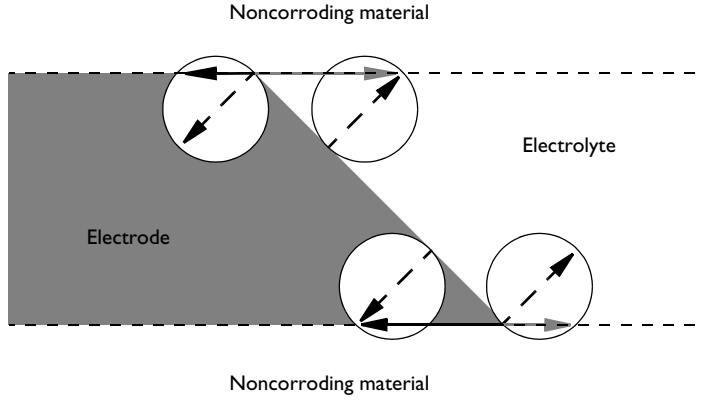
Figure 4-1: Gray/black arrows in whole stroke indicate the tangential electrode growth/dissolution velocities, $v_{t,\,\text{point}}$, at the three-phase intersections between an electrolyte, a deposition/dissolution electrode and a noncorroding material. Dashed arrows are the growth/dissolution velocities, v_{corr}, based on the corrosion rate expressions. Note that the tangential velocities depend on both the angle between the corroding surface and the noncorroding surface, as well as the direction of the normal velocity.

In the following, the boundary tangents are denoted by **t** (pointing from electrolyte to electrode) and the normal by **n** (pointing in the direction out from the electrolyte domain).

If the angle between the corroding boundary and the noncorroding boundary is larger than π, the tangential velocity is set to zero:

$$\text{if } (\mathbf{t}_{\text{noncorr}} \cdot \mathbf{n}_{\text{corr}} < 0) \qquad v_{t,\,\text{point}} = 0 \qquad\qquad (4\text{-}3)$$

Otherwise, (that is, if the angle between the corroding boundary and the noncorroding boundary is less than π), the following expressions are used:

Case 1:   if $v_{\text{corr}}\mathbf{n}_{\text{noncorr}} \cdot \mathbf{n}_{\text{corr}} > 0$ $v_{t,\,\text{point}} = v_{\text{corr}}/(\mathbf{t}_{\text{noncorr}} \cdot \mathbf{n}_{\text{corr}})$

Case 2:   if $v_{\text{corr}}\mathbf{n}_{\text{noncorr}} \cdot \mathbf{n}_{\text{corr}} < 0$ $v_{t,\,\text{point}} = v_{\text{corr}}(\mathbf{t}_{\text{noncorr}} \cdot \mathbf{n}_{\text{corr}})$ (4-4)

Note that Case 2 above results in a lower velocity in the normal direction of the corroding surface than the corrosion velocity, and that this will act toward forming a $\pi/2$ angle between the dissolving and the noncorroding boundary, a phenomena observed in experiments (Ref. 1).

On shared points (2D) and edges (3D) between a Non-Deforming Boundary and an Deforming Electrode Surface, the velocity of the corroding boundary is set according to the expressions above.

REFERENCE

1. J. Deconinck, "Mathematical Modeling of Electrode Growth," *J. Applied Electrochemistry*, vol. 24, 212–218, 1994.

5

Chemical Species Transport Interfaces

This chapter describes the physics interfaces found under the **Chemical Species Transport** branch ( ). It summarizes each physics interface including the different fields, material properties, and boundary conditions associated with them, and suggests how and when to apply it.

In this chapter:

- The Transport of Diluted Species Interface
- The Transport of Diluted Species in Fractures Interface
- The Chemistry Interface
- The Nernst-Planck-Poisson Equations Interface
- The Electrophoretic Transport Interface
- The Surface Reactions Interface
- Theory for the Transport of Diluted Species Interface
- Theory for the Electrophoretic Transport Interface
- Theory for the Surface Reactions Interface
- Theory for the Coupling of Mass Transport to Electrochemical Reactions

The Transport of Diluted Species Interface

The **Transport of Diluted Species (tds)** interface ( ), found under the **Chemical Species Transport** branch ( ), is used to calculate the concentration field of a dilute solute in a solvent. Transport and reactions of the species dissolved in a gas, liquid, or solid can be handled with this interface. The driving forces for transport can be diffusion by Fick's law, convection when coupled to a flow field, and migration, when coupled to an electric field.

The interface supports simulation of transport by convection and diffusion in 1D, 2D, and 3D as well as for axisymmetric components in 1D and 2D. The dependent variable is the molar concentration, c. Modeling multiple species transport is possible, whereby the physics interface solves for the molar concentration, c_i, of each species i.

SETTINGS

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

The **Name** is used primarily as a scope prefix for variables defined by the physics interface. Refer to such physics interface variables in expressions using the pattern `<name>.<variable_name>`. In order to distinguish between variables belonging to different physics interfaces, the `name` string must be unique. Only letters, numbers, and underscores (_) are permitted in the **Name** field. The first character must be a letter.

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

DOMAIN SELECTION

If any part of the model geometry should not partake in the mass transfer model, remove that part from the selection list.

TRANSPORT MECHANISMS

Mass transport due to diffusion is always included. Use the check boxes available under **Additional transport mechanisms** to control other transport mechanisms.

Note: Some of the additional transport mechanisms listed below are only available in certain products. For details see https://www.comsol.com/products/specifications/.

• By default, the **Convection** check box is selected. Clear the check box to disable convective transport.

• Select the **Migration in electric field** check box to activate transport of ionic species in an electric field. See further the theory section Adding Transport Through Migration.

| ! | Transport of ionic species in an electric field is available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability. |

Mass Transport in Porous Media

The **Mass transport in porous media** check box activates functionality specific to species transport in porous media. When selected, the following transport mechanisms are available:

• Select the **Dispersion in porous media** check box to activate the dispersion mechanism in porous media. See further Dispersion in the theory chapter.

• Select the **Volatilization in partially saturated porous media** check box to model volatilization in partially saturated domains. For more information see Theory for the Transport of Diluted Species Interface.

The following features are also enabled when selecting the **Mass transport in porous media** check box:

• Adsorption
• Fracture
• Partially Saturated Porous Media
• Porous Electrode Coupling
• Porous Media Transport Properties
• Reactive Pellet Bed
• Species Source

| ! | Note: Mass transport in porous media is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability. |

CONSISTENT STABILIZATION

To display this sections, click the **Show** button (👁) and select **Stabilization**.

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

    - **Do Carmo and Galeão** — the default option. This type of crosswind diffusion reduces undershoots and overshoots to a minimum but can in rare cases give equation systems that are difficult to fully converge.

    - **Codina**. This option is less diffusive compared to the Do Carmo and Galeão option but can result in more undershoots and overshoots. It is also less effective for anisotropic meshes. The Codina option activates a text field for the **Lower gradient limit** g_{lim}. It defaults to `0.1[mol/m^3]/tds.helem`, where `tds.helem` is the local element size.

• For both consistent stabilization methods, select an **Equation residual**. **Approximate residual** is the default and means that derivatives of the diffusion tensor components are neglected. This setting is usually accurate enough and is computationally faster. If required, select **Full residual** instead.

INCONSISTENT STABILIZATION

To display this section, click the **Show** button (👁) and select **Stabilization**. By default, the **Isotropic diffusion** check box is not selected, because this type of stabilization adds artificial diffusion and affects the accuracy of the original problem. However, this option can be used to get a good initial guess for underresolved problems.

ADVANCED SETTINGS

To display this section, click the **Show** button (👁) and select **Advanced Physics Options**. Normally these settings do not need to be changed. Select a **Convective term** — **Nonconservative form** (the default) or **Conservative form**. The conservative formulation should be used for compressible flow. See Convective Term Formulation for more information.

DISCRETIZATION

To display all settings available in this section, click the **Show** button (👁) and select **Advanced Physics Options**.

The **Compute boundary fluxes** check box is activated by default so that COMSOL Multiphysics computes predefined accurate boundary flux variables. When this option

is checked, the solver computes variables storing accurate boundary fluxes from each boundary into the adjacent domain.

If the check box is cleared, the COMSOL Multiphysics software instead computes the flux variables from the dependent variables using extrapolation, which is less accurate in postprocessing results but does not create extra dependent variables on the boundaries for the fluxes.

The flux variables affected in the interface are:

- ndflux_c (where c is the dependent variable for the concentration). This is the normal diffusive flux and corresponds to the boundary flux when diffusion is the only contribution to the flux term.
- ntflux_c (where c is the dependent variable for the concentration). This is the normal total flux and corresponds to the boundary flux plus additional transport terms, for example, the convective flux when you use the nonconservative form.

Also the **Apply smoothing to boundary fluxes** check box is available if the previous check box is checked. The smoothing can provide a more well-behaved flux value close to singularities.

For details about the boundary fluxes settings, see Computing Accurate Fluxes in the *COMSOL Multiphysics Reference Manual*.

The **Value type when using splitting of complex variables** setting should in most pure mass transfer problems be set to **Real**, which is the default. It makes sure that the dependent variable does not get affected by small imaginary contributions, which can occur, for example, when combining a Time Dependent or Stationary study with a frequency-domain study. For more information, see Splitting Complex-Valued Variables in the *COMSOL Multiphysics Reference Manual*.

DEPENDENT VARIABLES

The dependent variable name is the **Concentration** c by default. The names must be unique with respect to all other dependent variables in the component.

Add or remove species variables in the model and also change the names of the dependent variables that represent the species concentrations.

Enter the **Number of species**. Use the **Add concentration** (➕) and **Remove concentration** (≣ₓ) buttons as needed.

⊕

- 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 Media Transport Properties 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 Media Transport Properties** and **Partially Saturated Porous Media** 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 Media Transport Properties**, **No Flux** (the default boundary condition), and **Initial Values**. Then, from the **Physics** toolbar, add other nodes that implement, for example, boundary conditions, reaction rate expressions, and species sources. You can also right-click **Transport of Diluted Species in Porous Media** to select physics features from the context menu.

SETTINGS

The rest of the settings are the same as The Transport of Diluted Species Interface.

FURTHER READING

	• Theory for the Transport of Diluted Species Interface
🔍	• Domain, Boundary, and Pair Nodes for the Transport of Diluted Species Interface

	• *Variably Saturated Flow and Transport — Sorbing Solute*: Application Library path **Subsurface_Flow_Module/Solute_Transport/ sorbing_solute**
▥	Web link: https://www.comsol.com/model/ variably-saturated-flow-and-transport-sorbing-solute-490

Domain, Boundary, and Pair Nodes for the Transport of Diluted Species Interface

The Transport of Diluted Species Interface has the following domain, boundary, and pair nodes, listed in alphabetical order, available from the **Physics** ribbon toolbar

(Windows users), **Physics** context menu (Mac or Linux users), or by right-clicking to access the context menu (all users).

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

- Adsorption
- Concentration
- Electrode Surface Coupling
- Equilibrium Reaction
- Fast Irreversible Surface Reaction
- Flux
- Flux Discontinuity
- Fracture
- Inflow
- Initial Values
- Line Mass Source
- Mass-Based Concentrations
- No Flux
- Open Boundary
- Outflow
- Partially Saturated Porous Media
- Partition Condition

- Periodic Condition
- Point Mass Source
- Porous Electrode Coupling
- Porous Media Transport Properties
- Reaction Coefficients
- Reactions
- Reactive Pellet Bed
- Species Source
- Surface Reactions
- Surface Equilibrium Reaction
- Symmetry
- Thin Diffusion Barrier
- Thin Impermeable Barrier
- Transport Properties
- Turbulent Mixing
- Volatilization

Some features require certain add-on modules. For details see https://www.comsol.com/products/specifications/

> For axisymmetric components, COMSOL Multiphysics takes the axial symmetry boundaries (at $r = 0$) into account and automatically adds an **Axial Symmetry** node that is valid on boundaries representing the symmetry axis.

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

Transport Properties

The settings in this node are dependent on the check boxes selected under Transport Mechanisms on the Settings window for the Transport of Diluted Species interface. It includes only the sections required by the activated transport mechanisms. It has all the equations defining transport of diluted species as well as inputs for the material properties.

When the **Convection** check box is selected, the Turbulent Mixing subnode is available from the context menu as well as from the **Physics** toolbar, **Attributes** menu.

MODEL INPUTS

The temperature model input is always available. Select the source of the **Temperature**. For **User defined**, enter a value or expression for the temperature in the input field. This input option is always available.

You can also select the temperature solved for by a Heat Transfer interface added to the model component. These physics interfaces are available for selection in the **Temperature** list.

CONVECTION

If transport by convection is active, the velocity field of the solvent needs to be specified. Select the source of the **Velocity field**. For **User defined**, enter values or expressions for the velocity components in the input fields. This input option is always available.

You can also select the velocity field solved for by a Fluid Flow interface added to the model component. These physics interfaces are available for selection in the **Velocity field** list.

DIFFUSION

Select an option from the **Material** list. This selection list can only be used if a material has been added in the Materials node and if that material has a diffusion coefficient defined. Else, you need to type in the diffusivity in the **User Defined** edit field.

Enter the **Diffusion coefficient** D_c for each species. This can be a scalar value for isotropic diffusion or a tensor describing anisotropic diffusion. Select the appropriate tensor type — **Isotropic**, **Diagonal**, **Symmetric**, or **Full** that describes the diffusion transport, and then enter the values in the corresponding element (one value for each species).

Note that multiple species, as well as Migration in Electric fields (described below) is only available for certain COMSOL Multiphysics add-on products. See details: https://www.comsol.com/products/specifications/.

MIGRATION IN ELECTRIC FIELD

This section is available when the **Migration in electric field** check box is selected. From the **Electric potential** list, select the source of the electric field.

- Enter a value or expression for the **Electric potential** V, which is **User defined**; this input option is always available.

- Select the electric potential solved by an AC/DC-based interface that has also been added to the model.

- Select the electric potential defined or solved by Electrochemistry interface that has been added to the component.

By default the **Mobility** is set to be calculated based on the species diffusivity and the temperature using the **Nernst-Einstein relation**. For **User defined**, and under **Mobility**, select the appropriate scalar or tensor type — **Isotropic**, **Diagonal**, **Symmetric**, or **Full** — and type in the value of expression of the mobility $u_{m,c}$.

Enter the **Charge number** z_c (dimensionless, but requires a plus or minus sign) for each species.

The temperature (if you are using mobilities based on the Nernst-Einstein relation) is taken from **Model Inputs** section.

Note that the migration in electric fields feature is only available in some COMSOL products. See details: https://www.comsol.com/products/specifications/.

EXAMPLE MODELS

- *Separation Through Dialysis*: Application Library path
  Chemical_Reaction_Engineering_Module/Mixing_and_Separation/dialysis
  Web link: https://www.comsol.com/model/separation-through-dialysis-258

- *Transport in an Electrokinetic Valve*: Application Library path
  Microfluidics_Module/Fluid_Flow/electrokinetic_valve

  Web link: https://www.comsol.com/model/electrokinetic-valve-603

Turbulent Mixing

Use this node to account for the turbulent mixing of the chemical species caused by the eddy diffusivity. This node should typically be used when the specified velocity field corresponds to a RANS solution.

 This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

The subnode can added from the context menu (right-click the Transport Properties parent node), as well as from the **Physics** toolbar, **Attributes** menu, provided that **Convection** is selected as a transport mechanism.

TURBULENT MIXING PARAMETERS
Some physics interfaces provide the turbulent kinematic viscosity, and these appear as options in the **Turbulent kinematic viscosity** ν_T list. The list always contains the **User defined** option where any value or expression can be entered.

The default **Turbulent Schmidt number** Sc_T is 0.71 (dimensionless).

FURTHER READING
See the section About Turbulent Mixing in the *CFD Module User's Guide* (this link is available online or if you have the CFD Module documentation installed).

Initial Values

The **Initial Values** node specifies the initial values for the concentration of each species. These serve as an initial guess for a stationary solver or as initial conditions for a transient simulation.

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 menu. For an example, see the application *Fine Chemical Production in a Plate Reactor* as linked below.

This section is only available when the Mass Transport in Porous Media property is available and selected. See https://www.comsol.com/products/specifications/ for more details on availability.

When specifying reaction rates for a species in porous media, the specified reaction rate may have the basis of the total volume, the pore volume, or the volume of a particular phase.

- For **Total volume**, the reaction expressions in mol/(m^3·s) are specified per unit volume of the model domain (multiplied by unity).

- For **Pore volume**, the reaction expressions in mol/(m^3·s) are specified per unit volume of total pore space. The reaction expressions will be multiplied by the domain porosity, ε_p. (ε_p equals unity for nonporous domains.)

- For **Liquid phase**, the reaction expressions in mol/(m^3·s) are specified per unit volume of liquid in the pore space. The expressions will be multiplied by the liquid volume fraction θ. (θ equals ε_p for Saturated Porous Media domains).

- For **Gas phase**, the expressions are multiplied by the gas volume fraction $a_v = \varepsilon_p - \theta$. a_v equals 0 for Saturated Porous Media domains.

FURTHER READING

See the theory chapter on chemical species transport, starting with the section *Mass Balance Equation*.

⊞	- *Fine Chemical Production in a Plate Reactor*: Application Library path **Chemical_Reaction_Engineering_Module/ Reactors_with_Mass_and_Heat_Transfer/plate_reactor** Web link: https://www.comsol.com/model/ fine-chemical-production-in-a-plate-reactor-8589

No Flux

This node is the default boundary condition on exterior boundaries. It should be used on boundaries across which there is no mass flux, typically solid walls where no surface reactions occur. The condition applied for each species corresponds to

$$-\mathbf{n} \cdot (-D\nabla c) = 0$$

where $\mathbf{n}$ denotes the outward pointing normal of the boundary. When the mass transport includes migration of ionic species, the no flux condition is:

$$-\mathbf{n} \cdot (-D\nabla c - zu_m Fc\nabla\phi) = 0$$

CONVECTION

By default, the feature prescribes a vanishing flux due to diffusion and migration in an electric field. This is the appropriate no flux condition when the relative convective velocity at the boundary is zero. When the fluid velocity at the boundary is not equal to that of the boundary, it is often convenient to prescribe the total flux including the convection. To do this select **Include** in the **Convection** section.

When including the convection, the no flux condition prescribed is:

$$-\mathbf{n} \cdot (-D\nabla c + \mathbf{u}c) = 0$$

or

$$-\mathbf{n} \cdot (-D\nabla c - zu_m Fc\nabla\phi + \mathbf{u}c) = 0$$

when migration of ionic species is included.

Inflow

Use this node to specify all species concentrations at an inlet boundary.

If you want to specify the concentration of a subset of the partaking species, this can be done by using the Concentration node instead.

For the **Electroanalysis** interface, this node is available when you select the **Convection** check box on the physics interface **Settings** window.

CONCENTRATION

For the concentration of each species $c_{0,c}$ (SI unit: mol/m^3), enter a value or expression.

BOUNDARY CONDITION TYPE

The option **Concentration constraint** constrains the concentration values on the boundary by the use of pointwise constraints.

The other option, **Flux (Danckwerts)** can be used when the concentration at the boundary is not known, or when it varies in a non-trivial manner. This may, for example, be useful when reactions with high reaction rates occur in the vicinity of the

inlet. In this case the concentration far upstream of the boundary is instead prescribed. The **Flux (Danckwerts)** condition prescribes the total flux defined by the upstream concentration and the fluid velocity at the boundary.

CONSTRAINT SETTINGS

To display this section, click the **Show** button (👁) and select **Advanced Physics Options**. You can find details about the different constraint settings in the section Constraint Reaction Terms in the *COMSOL Multiphysics Reference Manual*.

FURTHER READING

See the theory chapter in the section Danckwerts Inflow Boundary Condition.

Outflow

Apply this condition at outlets boundaries where species should be transported out of the model domain by fluid motion or by an electric field (in the case of ions). It is assumed that convection and migration in an electric are the dominating transport mechanisms across the boundary, and therefore that the diffusive transport can be ignored, that is:

$$\mathbf{n} \cdot (-D\nabla c) = 0$$

Note that the **Convection** or the **Migration in electric field** transport mechanisms needs to be included for this node to be available.

Concentration

This condition node adds a boundary condition for the species concentration. For example, a $c = c_0$ condition specifies the concentration of species c.

CONCENTRATION

Individually specify the concentration for each species. Select the check box for the **Species** to specify the concentration, and then enter a value or expression in the corresponding field. To use another boundary condition for a specific species, click to clear the check box for the concentration of that species.

CONSTRAINT SETTINGS

To display this section, click the **Show** button (👁) and select **Advanced Physics Options**. You can find details about the different constraint settings in the section Constraint Reaction Terms in the *COMSOL Multiphysics Reference Manual*.

Flux

This node can be used to specify the species molar flux across a boundary. The flux can for example occur due to chemical reactions or a phase change at the boundary. The flux can also represent the transport to or from a surrounding environment currently not included model.

The prescribed flux of a species c is by default defined as

$$-\mathbf{n} \cdot (-D\nabla c) = J_0$$

where $\mathbf{n}$ denotes the outward pointing normal of the boundary. When the mass transport includes migration of ionic species, the flux is defined as:

$$-\mathbf{n} \cdot (-D\nabla c - z u_m F c \nabla \phi) = J_0$$

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.

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

$$-\mathbf{n} \cdot (-D\nabla c - z u_m F c \nabla \phi + \mathbf{u}c) = J_0$$

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

$$J_0 = k_c(c_b - c)$$

where k_c is a mass transfer coefficient and c_b is the bulk concentration, the typical concentration far into the surrounding exterior domain.

Symmetry

The **Symmetry** node can be used to represent boundaries where the species concentration is symmetric, that is, where there is no mass flux across the boundary.

This boundary condition is identical to that of the No Flux node.

Flux Discontinuity

This node represents a discontinuity in the mass flux across an interior boundary:

$$-\mathbf{n} \cdot [(\mathbf{J} + \mathbf{u}c)_u - (\mathbf{J} + \mathbf{u}c)_d] = N_0 \qquad \mathbf{J} = -D\nabla c - z u_m F c \nabla \phi$$

where the value N_0 (SI unit: mol/(m^2·s)) specifies the jump in total flux at the boundary. This can be used to model a boundary source, for example a surface reaction, adsorption or desorption.

FLUX DISCONTINUITY

In this section the jump in species flux (or surface source) is specified.

Select the Species check box for the species to specify and enter a value or expression for the material flux jump in the corresponding field. To use a different boundary condition for a specific species, click to clear the check box for the flux discontinuity of that species.

Partition Condition

The **Partition Condition** node can be used to prescribe the ratio between the concentration of a solute species in two different immiscible phases. It can for example be used on interior boundaries separating two liquid phases, a gas-liquid interface, or

on a boundary separating a liquid phase and a solid or porous media. For a species concentration c_i, the ratio between the concentration on the up side and on the down side of the boundary ($c_{i,\mathrm{u}}$ and $c_{i,\mathrm{d}}$ respectively) is defined as

$$K_i = \frac{c_{i,\mathrm{u}}}{c_{i,\mathrm{d}}}$$

in terms of a partition coefficient K_i. The up and down side of the selected boundary is indicated in the Graphics window. The arrows point from the down side into the up side.

	This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

PARTITION COEFFICIENT

Select the **Reverse direction** check box to reverse the direction of the arrows on the selected boundaries, and the corresponding definition of the up and down side concentration.

Use the associated input fields to prescribe the partition coefficient K_i.

FURTHER READING

For an example of using a partition condition, see this application example:

	Separation Through Dialysis: Application Library path **Chemical_Reaction_Engineering_Module/Mixing_and_Separation/dialysis**

Periodic Condition

The **Periodic Condition** node can be used to define periodicity for the mass transport between two sets of boundaries. The node prescribes continuity in the concentration and the mass flux between the "source" and the "destination" side respectively. Note that these names are arbitrary and does not influence the direction in which mass is transported. It is dictated by mass transfer equations in the adjacent domains.

The node can be activated on more than two boundaries, in which case the feature tries to identify two separate surfaces that each consist of one or several connected boundaries.

For more complex geometries, it might be necessary to add the **Destination Selection** subnode, which is available from the context menu (right-click the parent node) as well as from the **Physics** toolbar, **Attributes** menu. With this subnode, the boundaries that constitute the source and destination surfaces can be manually specified.

FURTHER READING

For an example of using a periodic condition, see this application example:

⊞	*The KdV Equation and Solitons*: Application Library path **COMSOL_Multiphysics/Equation_Based/kdv_equation**

Line Mass Source

The **Line Mass Source** feature models mass flow originating from a tube or line region with an infinitely small radius.

❗	This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

SELECTION

The **Line Mass Source** feature is available for all dimensions, but the applicable selection differs between the dimensions.

MODEL DIMENSION	APPLICABLE GEOMETRICAL ENTITY
2D	Points
2D Axisymmetry	Points not on the symmetry axis and the symmetry axis
3D	Edges

SPECIES SOURCE

Enter the source strength, $\dot{q}_{l,c}$, for each species (SI unit: mol/(m·s)). A positive value results in species injection from the line into the computational domain, and a negative value means that the species is removed from the computational domain.

Line sources located on a boundary affect the adjacent computational domains. This effect makes the physical strength of a line source located in a symmetry plane twice the given strength.

See the section Mass Sources for Species Transport.

Point Mass Source

The **Point Mass Source** feature models mass flow originating from an infinitely small domain around a point.

> ! | This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

SPECIES SOURCE

Enter the source strength, $\dot{q}_{p,c}$, for each species (SI unit: mol/s). A positive value results in species injection from the point into the computational domain, and a negative value means that the species is removed from the computational domain.

Point sources located on a boundary or on an edge affect the adjacent computational domains. This has the effect, for example, that the physical strength of a point source located in a symmetry plane is twice the given strength.

FURTHER READING

See the section Mass Sources for Species Transport.

Open Boundary

Use this node to set up mass transport across boundaries where both convective inflow and outflow can occur. On the parts of the boundary where fluid flows into the domain, an exterior species concentration is prescribed. On the remaining parts, where fluid flows out of the domain, a condition equivalent to the **Outflow** node is instead prescribed.

The direction of the flow across the boundary is typically calculated by a fluid flow interface and is provided as a model input to the Transport of Diluted Species interface.

> ⚠️ This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

EXTERIOR CONCENTRATION

Enter a value or expression for the **Exterior concentration**.

Thin Diffusion Barrier

Use this boundary condition to model a thin layer through which mass is transported by diffusion only. The node is applicable on interior boundaries and can be used to avoid meshing thin structures.

THIN DIFFUSION BARRIER

Specify the **Layer thickness**, d_s, and input a **Diffusion coefficient**, $D_{s,c}$, for each of the species included.

Thin Impermeable Barrier

This feature models a thin mass transfer barrier. It is available on interior boundaries and introduces a discontinuity in the concentration across the boundary. On each side, a no-flux condition is prescribed for the mass transport implying that it acts as a barrier. The feature can be used to avoid meshing thin structures.

Solving a model involving coupled fluid flow and mass transfer, the Thin Impermeable Barrier feature can be combined with an Interior Wall feature in order to model a thin solid wall.

Equilibrium Reaction

Use this node to model a reaction where the kinetics is assumed so fast that the equilibrium condition is fulfilled at all times. The node solves for an additional degree of freedom (the reaction rate R_{eq}) to fulfill the equilibrium condition at all times in all space coordinates.

If the **Apply equilibrium condition on inflow boundaries** check box is selected, the specified inflow concentration values in all active **Inflow** boundary nodes for the physics interface are modified to comply with the equilibrium condition.

> ⚠ • A necessary requirement for this is feature to be available is that two or more species are solved for by the interface.
> • This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

EQUILIBRIUM CONDITION
The list defaults to **Equilibrium constant** or select **User defined**. For either option, the **Apply equilibrium condition on inflow boundaries** check box is selected by default.

For **Equilibrium constant**, enter an **Equilibrium constant** K_{eq} (dimensionless). Also enter a value or expression for the **Unit activity concentration** C_{a0} (SI unit: 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.

FURTHER READING
See

• Equilibrium Reaction Theory
• Theory for the Coupling of Mass Transport to Electrochemical Reactions

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.

Specify the surface reaction rate J_0 of each species resulting from the reactions. Note that if you have the Chemistry interface available, provided with the Chemical Reaction Engineering Module, the reaction rate expressions can be automatically generated and picked up using the drop-down menu.

FURTHER READING

For an example of using the Surface Reactions node, see this application example:

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

Surface Equilibrium Reaction

Use this node to model an equilibrium reaction on a boundary (surface). The settings for this node are similar to Equilibrium Reaction. Note that a necessary requirement for this is feature to be available is that two or more species are solved for by the interface.

!	This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

Fast Irreversible Surface Reaction

This boundary node defines an irreversible reaction where the kinetics is so fast that the only factor limiting the reaction rate is the transport of a species to the reacting surface.

The node will set the **Rate limiting species concentration to zero** at the boundary, and balance the fluxes of the species participating in the reaction and the current densities according to the Stoichiometric Coefficients settings.

!	This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

Porous Electrode Coupling

Use this node to add a molar source in a domain that is coupled to one or multiple Porous Electrode Reaction nodes of an Electrochemistry Interface.

The molar source is calculated from the number of electrons, stoichiometric coefficients, and volumetric current densities of the coupled porous electrode reactions specified in the **Reaction Coefficients** subnodes.

In the Transport of Concentrated Species interface, the molar sources (or sinks) are multiplied by the species molar masses to obtain the corresponding mass sources.

Additional Reaction Coefficients subnodes are available from the context menu (right-click the parent node) as well as from the **Physics** toolbar, **Attributes** menu.

Note that if you are also modeling the momentum transport and expect a nonnegligible total mass source or sink, which is often the case in gas diffusion electrodes, you need to also add a corresponding Porous Electrode Coupling node in the Fluid Flow interface.

> ⚠️ This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

Reaction Coefficients

Add this node to the Electrode Surface Coupling and Porous Electrode Coupling features to define molar fluxes and sources based on electrode current densities in an **Electrochemistry** interface.

The molar flux or source is proportional to the stoichiometric coefficients and the current density according to Faraday's law.

Current densities from **Electrode Reaction** (i_{loc}, SI unit: A/m^2) or **Porous Electrode Reaction** nodes (i_v, SI unit: A/m^3) of any **Electrochemistry** interface in the model are available for selection as the **Coupled reaction**, and user-defined expressions are also supported.

Enter the **Number of participating electrons** n_m (dimensionless) and the **Stoichiometric coefficient** v_c (dimensionless) as explained in the theory section linked below.

Use multiple subnodes to couple to multiple reactions.

🔍	Theory for the Coupling of Mass Transport to Electrochemical Reactions

Electrode Surface Coupling

Use this node to define a flux boundary condition based on current densities of one or multiple Electrode Reaction nodes in an Electrochemistry interface.

The flux is proportional to the current densities and the stoichiometric coefficients according to Faraday's law as defined by summation over the Reaction Coefficients subnodes.

Note that if you are also modeling the momentum transport and expect a nonnegligible total mass flux over the boundary, which is often the case for gas diffusion electrodes, you need to also add a corresponding Electrode Surface Coupling node in the Fluid Flow interface.

⚠	This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

Porous Media Transport Properties

Use this node to model the concentration of diluted species transported through interstices in porous media. A part form convection and diffusion, the node contains functionality to include species evolution through adsorption, dispersion, and reaction.

⚠	This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

MODEL INPUTS

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.

MATRIX PROPERTIES

Use the **Porous material** list to define a material specifying the matrix properties on the current selection. By default the **Domain material** is used.

Specify the **Porosity,** ε_p (dimensionless) of the porous matrix. This is by default taken **From material**. Select **User defined** to instead enter a different value.

CONVECTION

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

Select a **Fluid material** (when available and applicable).

Specify the **Fluid diffusion coefficient** $D_{\mathrm{F,i}}$ (SI unit: m^2/s). Enter a value or expression for each of the species in the corresponding input field. The default is $1 \cdot 10^{-9}$ m^2/s.

Select the **Effective diffusivity model**: **Millington and Quirk model** (the default), **Bruggeman model**, **Tortuosity model**, or **User defined**. For **Tortuosity model**, enter a value for the tortuosity $\tau_{\mathrm{F,i}}$ (dimensionless). The default is 1.

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 effective 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 effective mobility $u_{me,c}$.

Enter the **Charge number** z_c for each species.

DISPERSION

This section is available when the **Dispersion in porous media** check box is selected on the **Settings** window for the physics interface.

Select the **Specify dispersion for each species individually** check box to specify the dispersion tensor D_D (SI unit: m²/s) for each species separately. The default is to use the same dispersion tensor D_D for all species.

Select an option from the **Dispersion tensor** list — **User defined** (the default) or **Dispersivity**. For **User defined**, use it to specify the dispersion components as user-defined constants or expressions. Select **Isotropic**, **Diagonal**, **Symmetric**, or **Full** based on the properties of the dispersion tensor.

Select **Dispersivity** when **Convection** has been added as the transport mechanism. Specify the dispersivities (SI unit: m) to define the dispersion tensor D_D (SI unit: m²/s) together with the velocity field **u**. 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.

Adsorption

Use this node to model adsorption of the fluid phase species onto the porous media surface. It is available as a subnode to the Porous Media Transport Properties and the Partially Saturated Porous Media 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

Use the **Porous material** list to define a material specifying the matrix properties on the current selection. By default the **Domain material** is used.

The density of the porous media is needed when modeling adsorption to the surface of the porous matrix. By default **Density** ρ is defined from the domain material.

ADSORPTION

Select a **Sorption type** — **Langmuir** (the default), **Freundlich**, **Toth**, **BET**, or **User defined** to specify how to compute c_P, the amount of species sorbed to the solid phase (moles per unit dry weight of the solid):

- For **Langmuir**:

$$c_P = c_{Pmax}\frac{K_L c}{1 + K_L c} \quad , \quad K_P = \frac{\partial c_P}{\partial c} = \frac{K_L c_{Pmax}}{(1 + K_L c)^2}$$

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)**:

$$c_{\mathrm{P}} \;=\; \frac{K_{\mathrm{B}} c_0 c}{(c_{\mathrm{S}} - c)\left(1 + (K_{\mathrm{B}} - 1)\dfrac{c}{c_{\mathrm{S}}}\right)}$$

and

$$K_P \;=\; \frac{\partial c_{\mathrm{P}}}{\partial c} \;=\; \frac{K_{\mathrm{B}} c_0 c_{\mathrm{S}}((K_{\mathrm{B}} - 1)c^2 + c_{\mathrm{S}}^2)}{(c - c_{\mathrm{S}})^2 (c_{\mathrm{S}} + (K_{\mathrm{B}} - 1)c)^2}$$

Enter a **BET constant** $K_{\mathrm{B},c}$ (dimensionless), a **Monolayer adsorption capacity** $c_{0,c}$ (SI unit: mol/kg), and an **Saturation concentration** $c_{\mathrm{S},c}$ (SI unit: mol/m^3).

• For **User defined**:

$$c_{\mathrm{P}} = f(c)$$

Enter an **Adsorption isotherm** $c_{\mathrm{P},c}$ (SI unit: mol/kg).

For more information, see Adsorption in the theory section.

FURTHER READING

See the theory chapter in the section Mass Balance Equation for Transport of Diluted Species in Porous Media.

Partially Saturated Porous Media

Use this node to model the concentration of diluted species transported by a liquid through in partially filled porous media. The interstices of the porous media contains the liquid carrier phase and gas pockets. A part from convection and diffusion, the node contains functionality to include species evolution through adsorption, dispersion, reaction, 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.

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.

MATRIX PROPERTIES

Use the **Porous material** list to define a material specifying the matrix properties on the current selection. By default the **Domain material** is used.

Specify the **Porosity,** ε_p (dimensionless) of the porous matrix. This is by default taken **From material**. Select **User defined** to instead enter a different value.

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 $\theta = s\varepsilon_p$.

For **Liquid volume fraction**, enter a value for θ (dimensionless) between 0 and the value of porosity. The saturation is then computed from the porosity and the liquid volume fraction as $s = \theta\varepsilon_p$.

Select a **Fluid fraction time change**: **Fluid fraction constant in time** (the default), **Time change in fluid 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).

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

Select a **Liquid material** from the list.

Specify the **Liquid diffusion coefficient** $D_{L,c}$ (SI unit: m^2/s). Enter a value or expression for each of the species in the corresponding input field. The default is $1 \cdot 10^{-9}$ m^2/s.

Select the **Effective diffusivity model, liquid**: **Millington and Quirk model** (the default), **Bruggeman model**, **Tortuosity model**, or **User defined**. For **Tortuosity model**, enter a value for $\tau_{L,c}$ (dimensionless). The default is 1.

When the **Volatilization in partially saturated porous media** check box is selected on the **Settings** window for the physics interface, also define the **Gas material**, **Gas diffusion coefficient**, and **Effective diffusivity model, gas**.

MIGRATION IN ELECTRIC FIELD

This section is available when the **Migration in electric field** check box is selected. It is similar to that in **Porous Media Transport Properties** feature. Select the source of electric field from the **Electric potential** list. The default selection to **Mobility** is the **Nernst-Einstein relation**.

DISPERSION

This section is available when the **Dispersion in porous media** check box is selected on the **Settings** window for the physics interface. The settings are the same as for Porous Media Transport Properties.

VOLATILIZATION

This section is available when the **Volatilization in partially saturated porous media** check box is selected on the **Settings** window for the physics interface.

Enter a value for the **Volatilization** $k_{G,c}$ (dimensionless) for each species.

Volatilization

This feature is available when the **Volatilization in partially saturated porous media** check box is selected on the **Settings** window for the physics interface.

Use this feature to model mass transfer at the boundary due to volatilization. The feature can be added on boundaries of a **Partially Saturated Porous Media** domain. In this case the porous media contains a liquid phase and a gas phase. 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

$$-\mathbf{n} \cdot \mathbf{J}_c = -h_c(k_{G,c}c - c_{\mathrm{Gatm},c})$$

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 **Partially Saturated Porous Media** domain.

Reactive Pellet Bed

Use this feature to model packed bed reactors with catalytic pellets. For details, see the section Theory for the Reactive Pellet Bed. By default, subnodes for Reactions and are added.

	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.

BED PARAMETERS

Here you can specify the bed porosity, which is the void fraction in the packed bed structure. Select **From densities** to calculate the porosity from the bed density and the individual pellet density. Select **User defined** to specify the porosity directly.

PELLET SHAPE AND SIZE

The default shape is spherical. Cylinders, flakes, and user-defined shapes can also be selected. A uniform pellet size or a discrete size distribution can be selected. Select a

Pellet size distribution — **Uniform size** (the default), **Two sizes**, **Three sizes**, **Four sizes**, or **Five sizes** to select up to five different particle sizes.

Depending on the shape selection, equivalent radii or volumes and surface areas will be required as input. If a size distribution is selected, the volume percentage of each size is required as input.

Note that different chemical reactions can be specified for each pellet size if a distribution is specified.

SURFACE SPECIES

In order to add surface species, click the **Add** button and enter the species name in the **Surface species** table. Added surface species are be available inside all pellet types defined in the **Pellet Shape and Size** section, but not in the bulk fluid.

For each pellet type, specify the **Reactive specific surface area**, $S_{b,reac}$ (SI unit: 1/m), corresponding to the surface area, per volume, available for surface reactions.

PELLET PARAMETERS

Enter a **Pellet porosity** ε_{pe} (dimensionless) to specify the porosity of the pellet internals.

Select **Diffusion model** — **Millington and Quirk model** (the default), **Bruggeman model**, **Tortuosity model**, or **User defined** to describe the effective correction of the diffusion coefficient in the pellet. In the case of the **Tortuosity model**, a value for the tortuosity τ_{pe} within the pellet is required.

Enter also the **Diffusion coefficient** $D_{pe,c}$ (SI unit: m^2/s). If a **User defined** diffusion model is selected, an **Effective diffusion coefficient** $D_{peff,c}$ (SI unit: m^2/s) is entered. The default value is $1 \cdot 10^{-9}$ m^2/s in both cases.

PELLET-FLUID SURFACE

For the coupling of concentration between the pellet internals and the surrounding fluid, two **Coupling type** options are available:

- **Continuous concentration**, assuming that all resistance to mass transfer to/from the pellet is within the pellet and no resistance to pellet-fluid mass transfer is on the bulk fluid side. The concentration in the fluid will thus be equal to that in the pellet pore just at the pellet surface: $c_{pe,i} = c_i$. This constraint also automatically ensures flux continuity between the internal pellet domain and the free fluid domain through so-called reaction forces in the finite element formulation.

- **Film resistance (mass flux)**: The flux of mass across the pellet-fluid interface into the pellet is possibly rate determined on the bulk fluid side, by film resistance. The resistance is expressed in terms of a film mass transfer coefficient, h_{Di}, such that:

$$N_{i,\text{inward}} = h_{D,i}(c_i - c_{\text{pe},i}).$$

The **Film resistance (mass flux)** option computes the inward surface flux, $N_{i,\text{inward}} = h_{D,i}(c_i - c_{\text{pe},i})$. h_{Di} is the mass transfer coefficient (SI unit: m/s) and is calculated with the default **Automatic** setting from a dimensionless **Sherwood number expression** or with **User defined** mass transfer coefficients.

The **Active specific surface area** (SI unit: m^{-1}) is required to couple the mass transfer between the pellets and the bed fluid. Select either the **Automatic** setting that calculates the specific surface area from the shape information given above. User defined is also available for explicit surface area specification.

The **Sherwood number expression** can be computed from three available expressions: **Frössling**, **Rosner**, and **Garner and Keey**. The Frössling equation is the default and probably the most commonly used for packed spheres. All of these are based on the dimensionless Reynolds, Re, and Schmidt, Sc, numbers, which are computed from **Density** and **Dynamic viscosity**. Select these to be taken either **From material** or choose the **User defined** alternative.

PELLET DISCRETIZATION

The extra dimension in the pellet needs to be discretized into elements. Select a **Distribution** — **Cubic root sequence** (the default), **Linear**, or **Square root sequence**. Enter the **Number of elements** N_{elem}.

CONSTRAINT SETTINGS

To display this section, click the **Show** button ( ) and select **Advanced Physics Options**. See the details about the different constraint settings in the section Constraint Reaction Terms in the *COMSOL Multiphysics Reference Manual*.

FURTHER READING

Theory for the Reactive Pellet Bed in the Theory section of this manual.

For an application using the Reactive Pellet Bed feature, see

	• *A Multiscale 3D Packed Bed Reactor*: Application Library path **Chemical_Reaction_Engineering_Module/Reactors_with_Porous_Catalysts/ packed_bed_reactor_3d** Web link: https://www.comsol.com/model/ a-multiscale-3d-packed-bed-reactor-17019

Reactions (Reactive Pellet Bed)

The Reactions subfeature to the Reactive Pellet Bed is used to define reaction terms to the transport within the reactive pellets. The feature also defines the corresponding averaged heat sources to be applied to heat transport in the bulk fluid.

DOMAIN SELECTION

From the **Selection** list, choose the domains on which to define rate expression or expressions that govern source terms in the transport equations.

Several reaction 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 using a value or an expression. One reaction rate per species and pellet type can be entered.

Note that if you have the *Chemistry* interface available, provided with the *Chemical Reaction Engineering Module*, the reaction rate expressions can be automatically generated and picked up using the drop-down menu. For an example, see the application *Fine Chemical Production in a Plate Reactor*.

SURFACE REACTION RATES

The section is available when one or more surface species have been added in the **Surface Species** section of the Reactive Pellet Bed feature.

Specify the rate expression $R_{\mathrm{surf},i}$ (SI unit: mol/(m^2·s)) corresponding to the surface reaction rate of each volumetric species i participating in the surface reaction. Furthermore, specify the surface reaction rates for the participating surface species in the corresponding table.

If several pellet types have been defined, one set of surface reaction rates per pellet type can be defined.

Note that if you have the *Chemistry* interface available, provided with the *Chemical Reaction Engineering Module*, the reaction rate expressions can be automatically generated and picked up using the drop-down menu.

HEAT SOURCE

Specify the heat source originating from the heat of reaction of the chemical reactions inside the pellet can be specified. Both heat sources from reactions in the fluid, and heat sources resulting from surface reactions can be defined. When using several pellet types, heat sources for each type can be added.

The heat sources are most conveniently picked up from a Chemistry feature that defines the reaction rate and the heat of reactions. In that case, the Rate expression can be selected from the drop-down menu. Else it can be set to User Defined.

The defined heat source can be used by a Heat Source feature in any of the heat transfer interfaces.

Species Source

In order to account for consumption or production of species in porous domains, the **Species Source** node adds source terms expressions S_i to the right-hand side of the species transport equations.

DOMAIN SELECTION

From the **Selection** list, choose the domains on which to define rate expression or expressions that govern the source term in the transport equations.

If there are several types of domains, with subsequent and different reactions occurring within them, it might be necessary to remove some domains from the selection. These are then defined in an additional **Species Source** node.

SPECIES SOURCE

Add a source term S_i (SI unit: mol/(m^3·s)) for each of the species solved for. Enter a value or expression in the field of the corresponding species.

Hygroscopic Swelling

The **Hygroscopic Swelling** multiphysics coupling node (⬕) is used for moisture concentration coupling between the Solid Mechanics interface and either the Transport of Diluted Species or Transport of Diluted Species in Porous Media interfaces.

Hygroscopic swelling is an effect of internal strain caused by changes in moisture content. This volumetric strain can be written as

$$\varepsilon_{hs} = \beta_h M_m (c_{mo} - c_{mo,ref})$$

where β_h is the coefficient of hygroscopic swelling, M_m is the molar mass, c_{mo} is the moisture concentration, and $c_{mo,ref}$ is the strain-free reference concentration.

This feature requires a license of either the MEMS Module or the Structural Mechanics Module. The multiphysics feature will appear automatically if both the Transport of Diluted Species and the Solid Mechanics interfaces are added to the same component. For the most current information about licensing, please see See https:// www.comsol.com/products/specifications/.

FURTHER READING

More information about how to use hygroscopic swelling can be found in Hygroscopic Swelling Coupling section in the *Structural Mechanics Module User's Guide*.

More information about multiphysics coupling nodes can be found in the section The Multiphysics Branch in the *COMSOL Multiphysics Reference Manual*.

Fracture

Use this node to model mass transport along thin fractures in porous media. The node assumes that the transport in the tangential direction along the fracture is dominant, as a result of lower flow resistance.

> ⚠ This feature is only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

FRACTURE PROPERTIES

Specify a value for the **Fracture thickness** d_{fr}.

MATRIX PROPERTIES

Use the **Porous material** list to define a material specifying the matrix properties on the current selection. By default the **Boundary material** is used.

Specify the **Porosity,** ε_p (dimensionless) of the porous matrix. This is by default taken **From material**. Select **User defined** to instead enter a different value.

CONVECTION

Select an option from the **Velocity field** list to specify the convective velocity along the fracture. For a consistent model, use a Fracture Flow feature in a Darcy's Law interface to compute the fluid flow velocity in the fracture.

For **User defined**, enter values or expressions for the velocity components in the table shown.

	The settings for the **Diffusion**, and **Dispersion** sections are the same as for Porous Media Transport Properties.

The Transport of Diluted Species in Fractures Interface

The **Transport of Diluted Species in Fractures (dsf)** interface ( ), found under the **Chemical Species Transport** branch ( ), is used to model the transport of a solute species along thin porous fractures, taking into account diffusion, dispersion, convection, and chemical reactions. The fractures are defined by boundaries and the solute species is assumed to be present in a solvent.

The interface supports simulation of species transport along boundaries in 2D and 3D, and axisymmetric components in 2D. The dependent variable is the molar concentration, c. Modeling multiple species transport is possible, whereby the physics interface solves for the molar concentration, c_i, of each species i.

> This interface is only available in a limited set of add-on products. For a detailed overview of which interfaces are available in each product, visit
> https://www.comsol.com/products/specifications/

SETTINGS

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

The **Name** is used primarily as a scope prefix for variables defined by the physics interface. Refer to such physics interface variables in expressions using the pattern `<name>.<variable_name>`. In order to distinguish between variables belonging to different physics interfaces, the `name` string must be unique. Only letters, numbers, and underscores (_) are permitted in the **Name** field. The first character must be a letter.

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

BOUNDARY SELECTION

If model geometry includes boundaries that should not be included in the mass transfer simulation, remove those from the selection list.

TRANSPORT MECHANISMS

Mass transport due to diffusion is always included. Use the **Convection** check box, available under **Additional transport mechanisms**, to control whether to also include convective transport.

CONSISTENT STABILIZATION

To display this sections, click the **Show** button (👁) and select **Stabilization**. Use this section to control the application of the available consistent stabilization methods; **Streamline diffusion** and **Crosswind diffusion**.

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

  - **Do Carmo and Galeão** — the default option. This type of crosswind diffusion reduces undershoots and overshoots to a minimum but can in rare cases give equation systems that are difficult to fully converge.

  - **Codina**. This option is less diffusive compared to the Do Carmo and Galeão option but can result in more undershoots and overshoots. It is also less effective for anisotropic meshes. The Codina option activates a text field for the **Lower gradient limit** g_{lim}. It defaults to `0.1[mol/m^3]/tds.helem`, where `tds.helem` is the local element size.

- For both consistent stabilization methods select an **Equation residual**. **Approximate residual** is the default and means that derivatives of the diffusion tensor components are neglected. This setting is usually accurate enough and is computationally faster. If required, select **Full residual** instead.

INCONSISTENT STABILIZATION

To display this section, click the **Show** button (👁) and select **Stabilization**. By default, the **Isotropic diffusion** check box is not selected, because this type of stabilization adds artificial diffusion and affects the accuracy of the original problem. However, this option can be used to get a good initial guess for underresolved 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*.

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** (≣ₓ) buttons as needed.

FURTHER READING

Q
- Mass Transport in Fractures in the theory section.
- Numerical Stabilization in the *COMSOL Multiphysics Reference Manual*.
- Domain, Boundary, and Pair Nodes for the Transport of Diluted Species Interface
- In the *COMSOL Multiphysics Reference Manual*, see Table 2-4 for links to common sections and Table 2-5 for common feature nodes. You can also search for information: press F1 to open the **Help** window or Ctrl+F1 to open the **Documentation** window.

Boundary, Edge, Point, and Pair Nodes for the Transport of Diluted Species in Fractures Interface

The Transport of Diluted Species 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).

- Adsorption
- Concentration
- Flux
- Fracture
- Inflow

- Initial Values
- No Flux
- Outflow
- Reactions
- Species Source

Adsorption

Use this node to model adsorption of the fluid phase species in onto the porous media surface of the fracture.

MATRIX PROPERTIES

Use the **Porous material** list to define a material specifying the matrix properties on the current selection. By default the **Domain material** is used. The density of the porous media is needed when modeling adsorption to the surface of the porous matrix. By default **Density** ρ is set to from domain material.

ADSORPTION

Select an **Adsorption isotherm** — **Langmuir** (the default), **Freundlich**, **Toth**, **BET**, or **User defined** to specify how to compute c_P, the amount of species sorbed to the solid phase (moles per unit dry weight of the solid):

- For **Langmuir**:

$$c_P = c_{Pmax}\frac{K_L c}{1 + K_L c} \qquad \frac{\partial c_P}{\partial c} = \frac{K_L c_{Pmax}}{(1 + K_L c)^2}$$

  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**:

$$c_P = K_F\left(\frac{c}{c_{ref}}\right)^N \qquad \frac{\partial c_P}{\partial c} = N\frac{c_P}{c} \qquad \text{Freundlich}$$

  Enter a **Freundlich constant** $k_{F,c}$ (SI unit: mol/kg), a **Freundlich exponent** $N_{F,c}$ (dimensionless), and a **Reference concentration** $c_{ref,c}$ (SI unit: mol/m^3).

- For **Toth**:

$$c_P = c_{Pmax}\frac{b_T c}{(1 + (b_T c)^{N_T})^{1/N_T}}$$

  and

$$\frac{\partial c_P}{\partial c} = c_{Pmax}b_T(1 + (b_T c)^{N_T})^{-\left(1 + \frac{1}{N_T}\right)}$$

Enter a **Toth constant** $b_{T,c}$ (SI unit: m^3/mol), a **Toth exponent** $N_{T,c}$ (dimensionless), and an **Adsorption maximum** $c_{p,max,c}$ (SI unit: mol/kg).

- For **BET (Brunauer-Emmett-Teller)**:

$$c_P = \frac{K_B c_0 c}{(c_S - c)\left(1 + (K_B - 1)\frac{c}{c_S}\right)}$$

and

$$\frac{K_B c_0 c_S ((K_B - 1)c^2 + c_S^2)}{(c - c_S)^2 (c_S + (K_B - 1)c)^2}$$

Enter a **BET constant** $K_{B,c}$ (dimensionless), a **Monolayer adsorption capacity** $c_{0,c}$ (SI unit: mol/kg), and an **Saturation concentration** $c_{S,c}$ (SI unit: mol/m^3).

- For **User defined**:

$$c_P = f(c)$$

Enter an adsorption isotherm $c_{P,c}$ (SI unit: mol/kg).

For more information, see Adsorption in the theory section.

FURTHER READING

See the theory chapter in the section Mass Balance Equation for Transport of Diluted Species in Porous Media.

Concentration

Use this node to specify the species concentration on a fracture boundary (applied in points in 2D and along edges in 3D). For example, a $c = c_0$ condition specifies the concentration of species c.

CONCENTRATION

Individually specify the concentration for each species. Select the check box for the **Species** to specify the concentration, and then enter a value or expression in the

corresponding field. To use another boundary condition for a specific species, click to clear the check box for the concentration of that species.

CONSTRAINT SETTINGS

To display this section, click the **Show** button ( ) and select **Advanced Physics Options**. You can find details about the different constraint settings in the section Constraint Reaction Terms in the *COMSOL Multiphysics Reference Manual*.

Flux

This node can be used to specify the species flux across a boundary of a porous fracture (applied in points in 2D and along edges in 3D). The flux of species c is defined as

$$\mathbf{n} \cdot (D_e \nabla c) = N_0$$

where N_0 is an arbitrary user-specified flux expression. For example, N_0 can represent a flux due to chemical reactions, or a phase change. A positive N_0 implies that the concentration inside the fracture increases.

INWARD FLUX

Specify the flux of each species individually. To use another boundary condition for a specific species, click to clear the check box for the mass fraction of that species.

Fracture

Use this node to model mass transport along thin fracture surfaces situated inside porous or solid material. The node assumes that the transport in the tangential direction of the fracture is dominant, as a result of lower flow resistance. Note that the fracture it self is modeled as porous.

MATRIX PROPERTIES

Use the **Porous material** list to define a material specifying the matrix properties on the current selection. By default the **Boundary material** is used.

Specify the **Porosity,** ε_p (dimensionless) of the porous matrix. This is by default taken **From material**. Select **User defined** to instead enter a different value.

CONVECTION

Select an option from the **Velocity field** list to specify the convective velocity along the fracture. For a consistent model, use The Fracture Flow Interface to compute the fluid flow velocity.

For **User defined**, enter values or expressions for the velocity components in the table shown.

The settings for the **Diffusion**, and **Dispersion** sections are the same as for Porous Media Transport Properties.

Inflow

Use this node to specify all species concentrations at a fracture inlet. The condition is applied in points in 2D and along edges in 3D

If you want to specify the concentration of a subset of the partaking species, this can be done by using the Concentration node instead.

CONCENTRATION

For the concentration of each species $c_{0,c}$ (SI unit: mol/m^3), enter a value or expression.

BOUNDARY CONDITION TYPE

This section in the settings is only available for some products. Search for "Inflow" on the page: https://www.comsol.com/products/specifications/ for more details on availability.

The option **Concentration constraint** constrains the concentration values on the boundary by the use of pointwise constraints. The other option, **Flux (Danckwerts)** can be more stable and fast to solve when high reaction rates are anticipated in the vicinity of the inlet. Oscillations on the solutions can also be avoided in such cases. The latter condition uses a flux boundary condition based on the velocity across the boundary and the concentration values. See further details in the theory section.

CONSTRAINT SETTINGS

To display this section, click the **Show** button ( ) and select **Advanced Physics Options**. You can find details about the different constraint settings in the section Constraint Reaction Terms in the *COMSOL Multiphysics Reference Manual*.

See the theory chapter in the section Danckwerts Inflow Boundary Condition.

No Flux

This node can be used to specify that the species flux across a boundary of a porous fracture is zero. The condition is applied in points in 2D and along edges in 3D.

Outflow

Set this condition at fracture outlets where species are transported out of the model domain by fluid motion. The condition is applied in points in 2D and along edges in 3D. It is assumed that convection is the dominating transport mechanism across outflow boundaries, and therefore that diffusive transport can be ignored, that is:

$$\mathbf{n} \cdot (-D_e \nabla c) = 0$$

Reactions

Use the **Reactions** node to account for the consumption or production of species through chemical reactions in the fracture. Define the rate expressions as required.

BOUNDARY SELECTION

From the **Selection** list, choose the boundaries on which to define rate expression or expressions that govern the source term in the transport equations.

Several reaction nodes can be used to account for different reactions in different parts of the fracture.

REACTION RATES

Add a rate expression R_i for species i. Enter a value or expression in the field. Note that if you have the *Chemistry* interface available, provided with the *Chemical Reaction Engineering Module*, the reaction rate expressions can be automatically generated and picked up using the drop-down menu.

REACTING VOLUME

When specifying reaction rates for a species in a fracture, the specified reaction rate may have the basis of the pore volume of the fracture, or the total volume.

- For **Total volume**, the reaction expressions in are specified per unit volume of the fracture. The reaction expressions will be multiplied by the fracture thickness d_{fr}.

- For **Pore volume**, the reaction expressions in $\mathrm{mol}/(\mathrm{m}^3 {\cdot} \mathrm{s})$ 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 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 on the **Settings** window for the Chemistry interface.

SETTINGS

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

The **Name** is used primarily as a scope prefix for variables defined by the physics interface. Refer to such physics interface variables in expressions using the pattern `<name>.<variable_name>`. In order to distinguish between variables belonging to different physics interfaces, the `name` string must be unique. Only letters, numbers, and underscores (_) are permitted in the **Name** field. The first character must be a letter.

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

MODEL INPUT

This section sets the **Temperature, Pressure** and **Electrode potential** (only available with a Batteries & Fuel Cells, Corrosion, Electrochemistry or Electrodeposition 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.

CALCULATE THERMODYNAMIC PROPERTIES

Select the **Calculate thermodynamic properties** check box to enable the interface to compute thermodynamic properties, especially critical if the reaction kinetics are defined at nonisothermal conditions.

MIXTURE PROPERTIES

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

The **Thermodynamics** check box is enabled 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

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

Select **Diluted species** from the **Mixture type** list to use the concentration variables from a Transport of Diluted Species interface. The same setting should be used for any other interface solving for species concentrations using a diluted species assumption. Enter the names of the dependent variables in the **Molar concentration** column.

Select **Concentrated species** from the **Mixture type** list to use the mass fractions from a Transport of Concentrated Species interface. Enter the names of the dependent variables in the **Mass fraction** column.

Surface Species
Specify the concentration of surface species in the table in this section. 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
Specify the concentration of solid species in the table in this section.

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

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

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

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

The Reaction Rate Variable
The name of the reaction rate variables for each species generated by the interface can be seen in the **Reaction Rate** column of the **Species concentration input** table. The syntax of the reaction rate variables depend on the **Species type** selected in the Species **Settings** window. **Bulk species** and **Solvent** use the syntax R_*speciesname*, while **Surface species** uses R_*speciesname*_surf. Selecting **Concentrated species** for the **Mixture type**, the base of syntax for the reaction rate is changed to Rw_*speciesname*.

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 post processing 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.

EXTRA DIMENSION

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

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

ACTIVITY

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

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

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 on the **Chemistry** toolbar click **Reaction**.

REACTION FORMULA

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

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 a species is:

$$R_i = \nu_i r \tag{5-1}$$

• If the reaction is at **Equilibrium**, 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**.

The **Automatic Reaction rate** expression is set up according to the mass action law:

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

$$r_j = k_j^f \prod_{i \,\in\, \text{react}} c_i^{-\nu ij}$$

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

$$r_j = k_j^f \prod_{i \,\in\, \text{react}} c_i^{-\nu ij} - k_j^r \prod_{i \,\in\, \text{prod}} c_i^{\nu ij} \tag{5-2}$$

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 5-2).

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.

$$k^f = A^f (T/T_{\text{ref}})^{n^f} \exp(-E^f/(R_g T))$$

$$k^r = A^r (T/T_{\text{ref}})^{n^{rf}} \exp(-E^r/(R_g T))$$

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 (SI unit: $(\text{m}^\beta/\text{mol})^{\alpha-1}$/s, where α equals the order of the reaction and β is 3 or 2 for volumetric or surface reactions, respectively)
- **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:

$$K_{\text{eq}j} = \frac{\prod\limits_{i\,\in\,\text{prod}} c_i^{\nu ij}}{\prod\limits_{i\,\in\,\text{react}} c_i^{-\nu ij}}$$

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. This settings requires that the **Calculate thermodynamic properties** in the corresponding section is selected.

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 has information about thermodynamic properties that relate to a selected reaction and is available when the Feature Nodes Available for the Chemistry Interface check box is selected for the Chemistry interface. 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:

$$H_j = \sum_{i \in \text{prod}} v_{ij}h_i - \sum_{i \in \text{react}} (-v_{ij})h_i \qquad (5\text{-}3)$$

Entropy of Reaction

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

$$S_j = \sum_{i \in \text{prod}} v_{ij}s_i - \sum_{i \in \text{react}} (-v_{ij})s_i \qquad (5\text{-}4)$$

In Equation 5-3 and Equation 5-4, 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 5-3 and Equation 5-4 to equate the Gibbs free energy of reaction enables the equilibrium constant to be expressed according to Equation 5-3.

Heat Source of Reaction

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

$$Q_j = -H_j r_j$$

Ⓠ   Using the Reaction Node

Species

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

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

SPECIES NAME

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

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

Ⓠ   Creating Valid Species Names and Labeling

SPECIES TYPE

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

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

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

GENERAL PARAMETERS

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

Edit, if necessary, the species **Molar mass** M and the ionic **Charge** z of the species in question.

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 in the reactor since the reaction of the species can depend both on bulk reaction R and surface reaction R_{ads} rates. For a surface species, only the surface reaction rate R_{ads} appears.

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).

SPECIES CONCENTRATION/ACTIVITY

To account for non-ideality in the fluid mixture, adjust the activity coefficient in the **Activity coefficient** input field. This input field is only shown if activity instead of

concentration has been chosen in the interface, that is, the **Use activities** check box is selected on the Chemistry interface **Settings** window

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

SPECIES THERMODYNAMIC EXPRESSIONS

The parameters utilized for calculation of thermodynamic mixture and reaction properties are set in this section. It is accessed when the Feature Nodes Available for the Chemistry Interface check box is selected on the Chemistry interface **Settings** window, that is, temperature dependence is accounted for.

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 on 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 Batteries & Fuel Cells, Corrosion, Electrochemistry or Electrodeposition 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.

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 Thermodynamic Properties option 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 Electrochemistry 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.

Iftheequilibrium 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 Electrochemistry 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

$$E_{therm} = -\frac{\Delta_r H}{nF} \tag{5-5}$$

using the Species enthalpies.

	• Electrode Reactions Theory
⑦	• Electrode Kinetics Expressions

Electrode Reaction Group

To add an **Electrode Reaction Group** node (⚗) either right-click the **Chemistry** node or on 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 Batteries & Fuel Cells, Corrosion, Electrochemistry or Electrodeposition module license.

Reversible Reaction Group

The **Reversible Reaction Group** node (![icon]) 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 (Feature Nodes Available for the Chemistry Interface check box is selected), right-click to add a Reaction Thermodynamics subnode or select it from the **Chemistry** toolbar, **Attributes** menu. In it, the Enthalpy of Reaction (J/mol) for each reaction can be specified.

REACTION TABLE

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

- In general, use the **Move Up** (⬆), **Move Down** (⬇), and **Delete** (≡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.

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

CREATE REACTION AND SPECIES

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

Equilibrium Reaction Group

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

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

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

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

- In general, use the **Move Up** (↑), **Move Down** (↓), and **Delete** (≡) buttons and the fields under tables to edit the table contents. Or right-click a table cell and select **Move Up**, **Move Down**, or **Delete**.

- The **Add** button (+) adds default reactant, A, and product, B, with a default. Click the corresponding field to edit the reactant, product, or parameters. After editing the Species Group node is also updated. It is created together with the reaction group.

- You can save the parameters to a text file to reuse in other models. Click the **Save to File** button (▣) and enter a **File name** in the **Save to File** dialog box, including the extension .txt. Click **Save** to store the parameters in a text file or in a Microsoft Excel Workbook spreadsheet if the license includes LiveLink™ *for* Excel®. The information is saved in space-separated columns in the same order as displayed on screen. When saving to Excel, an **Excel Save** dialog box appears where you can specify the sheet and range and whether to overwrite existing data or include a header.

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

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

Species Group

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

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

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

Reaction Thermodynamics

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

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

Species Activity

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

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

Species Thermodynamics

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

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

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 The Transport of Diluted Species Interface ( ) (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 Space Charge Density Coupling ( ) 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 Potential Coupling ( ) 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.

Q	• 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 **Corrosion_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 auto-ionization reaction.

The physics interface can simulate most forms of electrophoresis modes, such as zone electrophoresis, isothachophoresis, 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.

	For 2D components, enter a value or expression for the out-of-plane **Thickness** d (SI unit: m). The value of d determines the size of the domain perpendicular to the modeled 2D cross section. This value yields, for example, the correct total current when the current density is obtained from a 2D simulation.

CROSS SECTIONAL AREA

	For 1D components, enter a **Cross sectional area** A_c (SI unit: m^2) to define a parameter for the area of the geometry perpendicular to the 1D component. The value of this parameter is used, among other things, to automatically calculate the total current from the current density vector. The analogy is valid for other fluxes. The default is 1 m^2.

TRANSPORT MECHANISMS

Mass transport due to diffusion and migration is always included. Use the check boxes available under **Additional transport mechanisms** to control other transport mechanisms.

• By default, the **Convection** check box is selected. Clear the check box to disable convective transport.

• The **Mass transfer in porous media** check box activates functionality specific to species transport in porous media. When selected, the Porous Matrix Properties node can be added to a domain to specify the electrolyte volume fraction and tortuosity, and the Effective Transport Parameter Correction sections are enabled in the species nodes.

CONSISTENT STABILIZATION

To display this sections, click the **Show More Options** button ( ) and select **Stabilization** in the **Show More Options** dialog box.

• When the **Crosswind diffusion** check box is selected, a weak term that reduces spurious oscillations is added to the transport equation. The resulting equation system is always nonlinear.

• For both **Streamline diffusion** and **Crosswind diffusion**, select an **Equation residual**. **Approximate residual** is the default and means that derivatives of the diffusivity are

neglected. This setting is usually accurate enough and is computationally faster. If required, select **Full residual** instead.

INCONSISTENT STABILIZATION

To display this section, click the **Show More Options** button (👁) and select **Stabilization** in the **Show More Options** dialog box. By default, the **Isotropic diffusion** check box is not selected, because this type of stabilization adds artificial diffusion and affects the accuracy of the original problem. However, this option can be used to get a good initial guess for under-resolved problems.

ADVANCED SETTINGS

To display this section, click the **Show More Options** button (👁) and select **Advanced Physics Options** in the **Show More Options** dialog box. Normally these settings do not need to be changed. Select a **Convective term** — **Nonconservative form** (the default) or **Conservative form**. The conservative formulation should be used for compressible flow.

DISCRETIZATION

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

The concentration variables are set to use Linear elements by default.

The potential variable is set to use Quadratic elements by default.

The **Compute boundary fluxes** check box is activated by default so that COMSOL Multiphysics computes predefined accurate boundary flux variables. When this option is checked, the solver computes variables storing accurate boundary fluxes from each boundary into the adjacent domain.

If the check box is cleared, the COMSOL Multiphysics software instead computes the flux variables from the dependent variables using extrapolation, which is less accurate in postprocessing results but does not create extra dependent variables on the boundaries for the fluxes.

The flux variables affected in the interface are:

- <name>.nIl, where <name> is the name of the interface (default is el), set on the interface top node. This is the normal electrolyte current density.
- <name>.ntflux_<species_name> is the **Species name** (see Common Settings for the Species Nodes in the Electrophoretic Transport Interface below). This is the normal total flux for each species.

Also the **Apply smoothing to boundary fluxes** check box is available if the previous check box is checked. The smoothing can provide a more well-behaved flux value close to singularities.

For details about the boundary fluxes settings, see Computing Accurate Fluxes in the *COMSOL Multiphysics Reference Manual*.

Regarding the **Value type when using splitting of complex variables**, see Splitting Complex-Valued Variables in the *COMSOL Multiphysics Reference Manual*.

DEPENDENT VARIABLES

The dependent variable name for the electrolyte potential variable is phil by default.

The name of the concentration dependent variables are named as el.xxx, where the el is the name of the interface as set above, and the xxx string is controlled by the **Species name** setting on the individual species nodes.

FURTHER READING

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

Common Settings for the Species Nodes in the Electrophoretic Transport Interface

The interface features the following species nodes, applicable on the domain level:

- Ampholyte
- Fully Dissociated Species
- Uncharged Species
- Weak Acid
- Weak Base

Each species node add a dependent variable for the concentration. The initial and boundary condition, as well as adding additional source reaction terms, for each species concentration is controlled by adding subnodes to the species nodes:

• Concentration

• Flux

• Inflow

• Initial Concentration

• No Flux

• Outflow

• Species Source

The Ampholyte, Weak Acid and Weak Base are dissociation species and may define an arbitrary number of dissociation steps. Each dissociation step is defined by it's 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 a ion-selective membrane or a gel. When the check box is enabled the concentration of the species is not added as a dependent variable to the model; instead the concentration will be set to the value provided in the **Concentration** field. The contribution to the electrolyte current for immobile species is zero.

Diffusion and Migration Settings

All species, except when the **Immobile Species** check box has been enabled, may be transported by diffusion, and charged species are also transported by migration in the electric field.

For dissociation species you may choose to set the transport parameters to be the **Same for all species** appearing in the different dissociation steps, or you may use **Individual** settings for each subspecies.

Typically the mobilities and diffusivities for small species are related by the **Nernst-Einstein relation**, and when this relation is enabled you can choose whether to specify either the **Diffusivity** (SI unit: m^2/s) or the **Mobility** (SI-unit: s·mol/kg). The **Debye-Hückel-Henry** relation is commonly used for larger molecules, such as proteins.

Note: There are other definitions of the migration transport equations in literature which use mobilities expressed in $m^2/(V \cdot s)$, whereas COMSOL Multiphysics uses s·mol/kg. To convert mobilities expressed in $m^2/(V \cdot s)$ to the corresponding values in s·mol/kg, you typically divide by the Faraday constant, F_const (about 96,485 C/mol).

EFFECTIVE TRANSPORT PARAMETER CORRECTION

If **Mass transfer in porous media** is enabled on the interface top node, you may use the settings of this section in the species nodes to account for the changed mass transport in a porous domain due to the lowered porosity and the increased tortuosity.

The default correction model is **Bruggeman**, which multiplies the diffusivity and mobility values by the porosity to the power of 1.5. The porosity of a domain is set by the Porous Matrix Properties node.

IONIC STRENGTH CONTRIBUTION

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

The **Debye-Hückel-Henry** relation makes use of the ionic strength for calculating the species mobility from the diffusivity. All charged species contribute to the ionic strength, either assuming the species contributing to an **Ideal solution** or by using the **Lindestrøm-Lang** assumption. The latter is usually used for macromolecules.

Domain, Boundary, and Pair Nodes for the Electrophoretic Transport Interface

The interface has the following domain, boundary, and pair nodes, listed in alphabetical order, available from the **Physics** ribbon toolbar (Windows users), **Physics** context menu (Mac or Linux users), or by right-clicking to access the context menu (all users).

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

- Ampholyte
- Concentration
- Current
- Current Density
- Current Source
- Flux
- Fully Dissociated Species
- Inflow
- Initial Concentration
- Initial Potential
- Insulation
- No Flux
- Outflow
- Porous Matrix Properties
- Potential
- Protein
- Species Source
- Solvent
- Uncharged Species
- Weak Acid
- Weak Base

	For axisymmetric components, COMSOL Multiphysics takes the axial symmetry boundaries (at $r = 0$) into account and automatically adds an **Axial Symmetry** node that is valid on boundaries representing the symmetry axis.

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

Solvent

The settings of this node are used to define the properties of the aqueous solvent.

If Convection is enabled on the interface top node, you can specify the **Velocity field** (m/s) as user defined input using analytical expressions or the velocity field variables solved for by a separate physics interface.

The Solvent node automatically defines the concentration variables and for protons (<name>.cH) and hydroxide ions (<name>.cOH), and the corresponding flux expressions. See Diffusion and Migration Settings for how to set up the transport parameters for the proton and hydroxide ions.

In the **Solvent Properties** section you can modify the **Dynamic viscosity** (Pa·s) and **Relative permittivity** (unitless) values. The **Built in** and default values are applicable to water. These parameters are used when calculating mobilities according to the **Debye-Hückel-Henry** relation in the species nodes.

In the **Water Self-Ionization** section you can change the default **Built in** expression for the **Water self-ionization constant**, pK_w (unitless), to any user defined expression.

Porous Matrix Properties

Use this node, available if **Mass transfer in porous media** has been enabled on the interface top-node, to define the **Porosity** (electrolyte volume fraction) and **Tortuosity** of a domain.

The porosity should be a number between 0 and 1.

Fully Dissociated Species

Use this node to define a fully dissociated charged species, such as strong bases and acids.

The **Charge number**, Z_0 (unitless), defines the species charge.

See also Common Settings for the Species Nodes in the Electrophoretic Transport Interface and Diffusion and Migration Settings.

Uncharged Species

Use this node to define a species that does not carry any charge, nor is impacted by the electric field.

See also Common Settings for the Species Nodes in the Electrophoretic Transport Interface and Diffusion and Migration Settings.

Weak Acid

The **Weak acid** node supports multiple dissociation steps, where the acid of the first dissociation step is uncharged.

The species may be either **Monoprotic,** subject to one dissociation step only, or **Polyprotic**. For the latter case any **Number of dissociation steps** larger than one may be used.

See also Common Settings for the Species Nodes in the Electrophoretic Transport Interface and Diffusion and Migration Settings.

Weak Base

The **Weak base** node supports multiple dissociation steps, where the base of the last dissociation step is uncharged.

The species may be either **Monoprotic,** subject to one dissociation step only, or **Polyprotic**. For the latter case any **Number of dissociation steps** larger than one may be used.

Note that the 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**, $\overline{Z}$ (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 $\overline{Z}$.

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,** $\phi_{1, \text{bnd}}$ (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 a electrolyte reservoir.

No Flux

This node may be added as a subnode to any species node. See also Common Settings for the Species Nodes in the Electrophoretic Transport Interface.

This node is the default boundary condition on exterior boundaries. It represents boundaries where no mass flows in or out of the boundaries. Hence, the total flux is zero.

Flux

This node may be added as a subnode to any species node. See also Common Settings for the Species Nodes in the Electrophoretic Transport Interface.

This node can be used to specify the species inward flux across a boundary. The flux can represent a flux from or into a much larger surrounding environment, a phase change, or a flux due to chemical reactions.

INWARD FLUX

Enter a value or expression for the species mass flux J_0. Use a minus sign when specifying a flux directed out of the system.

External convection

Set **Flux type** to **External convection** to prescribe a flux to or from an exterior domain (not modeled) assumed to include convection. The exterior can for example include a forced convection to control the temperature or to increase the mass transport. In this case the prescribed mass flux corresponds to

$$J_0 = k_c(c_b - c)$$

where k_c is a mass transfer coefficient and c_b is the bulk concentration, the typical concentration far into the surrounding exterior domain.

Inflow

This node is available when you select the **Convection** check box on the physics interface **Settings** window.

Use this node to specify the species concentrations at an inlet boundary.

BOUNDARY CONDITION TYPE

The option **Concentration constraint** constrains the concentration values on the boundary by the use of pointwise constraints. When using this option the boundary condition is identical to the Concentration node.

The other option, **Flux (Danckwerts)** can be more stable and fast to solve when high reaction rates are anticipated in the vicinity of the inlet. Oscillations on the solutions can also be avoided in such cases. The latter condition uses a flux boundary condition based on the velocity across the boundary and the concentration values.

Outflow

Set this condition at outlets where species are transported out of the model domain by migration or fluid motion. It is assumed that migration and convection is the dominating transport mechanism across outflow boundaries, and therefore that diffusive transport can be ignored, that is:

$$\mathbf{n} \cdot (-D\nabla c) = 0$$

The Surface Reactions Interface

The **Surface Reactions (sr)** interface ( ), found under the **Chemical Species Transport** branch ( ) when adding a physics interface, is used to model the chemical reactions of surface and bulk species on a boundary. Surface species can be transported in the tangential direction of the surface by Fick's law whereas bulk species are assumed to be immobile on the surface.

The physics interface supports simulation of surface reactions on boundaries in 1D, 2D, and 3D as well as for axisymmetric components in 1D and 2D. The dependent variables are the surface concentrations, $c_{s,i}$ (SI unit: mol/m^2) and the bulk concentrations, $c_{b,i}$ (SI unit: mol/m^2).

When this physics interface is added, these default nodes are also added to the **Model Builder** — **Surface Properties**, **No Flux**, and **Initial Values**. Then, from the **Physics** toolbar, add other nodes that implement, for example, boundary conditions. You can also right-click **Surface Reactions** to select physics features from the context menu.

SETTINGS

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

The **Name** is used primarily as a scope prefix for variables defined by the physics interface. Refer to such physics interface variables in expressions using the pattern `<name>.<variable_name>`. In order to distinguish between variables belonging to different physics interfaces, the `name` string must be unique. Only letters, numbers, and underscores (_) are permitted in the **Name** field. The first character must be a letter.

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

DEPENDENT VARIABLES

Add or remove species and also change the names of the dependent variables that represent the species concentrations. Note that the names can be changed but the names of fields and dependent variables must be unique within a model.

Enter the **Number of surface species**. Use the **Add surface concentration** ( ) and **Remove surface concentration** ( ) buttons as needed. The same number of **Surface concentrations** `cs`, `cs2`, `cs3`, … are then listed in the table.

Enter the **Number of bulk species**. Use the **Add bulk concentration** (➕) and **Remove bulk concentration** (▤) buttons as needed. The same number of **Bulk concentrations** cb, cb2, cb3, … are then listed in the table.

DISCRETIZATION

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

CONSISTENT AND INCONSISTENT STABILIZATION

To display these sections, click the **Show More Options** button (👁) and select **Stabilization** in the **Show More Options** dialog box.

By default the **Compensate for boundary stretching** check box is selected for the Surface Properties node. This section is then used to stabilize the tangential mesh velocity term.

When the **Compensate for boundary stretching** check box is cleared (not selected), and for fixed geometries or moving geometries, the stabilization has no effect.

See Surface Reaction Equations on Deforming Geometries for more information.

🔍
- Boundary, Edge, Point, and Pair Nodes for the Surface Reactions Interface
- Theory for the Surface Reactions Interface

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

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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.

Q 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: mol/(m^2·s)).

CONSTRAINT SETTINGS

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

Theory for the Transport of Diluted Species Interface

The Transport of Diluted Species Interface provides a predefined modeling environment for studying the evolution of chemical species transported by diffusion and convection as well as migration due to an electric field. The physics interface assumes that all species present are dilute; that is, that their concentration is small compared to a solvent fluid or solid. As a rule of thumb, a mixture containing several species can be considered dilute when the concentration of the solvent is more than 90 mol%. Due to the dilution, mixture properties such as density and viscosity can be assumed to correspond to those of the solvent.

When studying mixtures that are not dilute, the mixture and transport properties depend on the composition, and a different physics interface is recommended. See The Transport of Concentrated Species Interface 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 The Transport of Diluted Species in Porous Media Interface:

- Adsorption
- Convection in Porous Media
- Diffusion in Porous Media
- Dispersion

- Mass Balance Equation for Transport of Diluted Species in Porous Media
- Mass Transport in Fractures
- Reactions

Mass Balance Equation

The default node attributed to the Transport of Diluted Species interface models chemical species transport through diffusion and convection and solves the mass conservation equation for one or more chemical species i:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{J}_i + \mathbf{u} \cdot \nabla c_i = R_i \tag{5-6}$$

Equation 5-6 in its form above includes the transport mechanisms diffusion and convection. If *Migration in Electric Field* is activated (only available in some add-on products), the migration mechanism will be added to the equation as well. See more details in the section Adding Transport Through Migration.

- c_i is the concentration of the species (SI unit: mol/m^3)
- D_i denotes the diffusion coefficient (SI unit: m^2/s)
- R_i is a reaction rate expression for the species (SI unit: mol/(m^3·s))
- $\mathbf{u}$ is the mass averaged velocity vector (SI unit: m/s)
- $\mathbf{J}_i$ is the mass flux diffusive flux vector (SI unit: mol/(m^2·s))

The mass flux relative to the mass averaged velocity, $\mathbf{J}_i$ (SI unit: mol/(m^2·s)), is associated with the mass balance equation above and used in boundary conditions and flux computations. The Transport of Diluted Species interface always includes mass transport due to molecular diffusion. In this case the mass flux $\mathbf{J}_i$ defines the diffusive flux vector

$$\mathbf{J}_i = -D\nabla c \tag{5-7}$$

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 5-6 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 5-6), 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, v_i (dimensionless), of the reaction; the species activities of the reacting species a_i (dimensionless); and an equilibrium constant, K_{eq} (1) according to:

$$K_{eq} = \frac{\prod_{i \in \text{products}} a_i^{v_i}}{\prod_{i \in \text{reactants}} a_i^{-v_i}}$$

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 Modules Chemical Engineering, Corrosion, Electrochemistry, Electrodeposition, and Batteries and Fuel Cells.

🗒	$\gamma_{c,i}$ is set to unity when the Equilibrium constant is selected on the Settings window. For nonunity activity coefficients, a user defined equilibrium condition can be used.

EQUILIBRIUM REACTIONS AND INFLOW BOUNDARY CONDITIONS

Contradictory constraints arise if the boundary conditions for concentrations or activities are set so that the domain equilibrium condition is not fulfilled. Special treatment is therefore needed at Inflow boundaries, where the concentrations are set for all species in the mass transport interfaces.

One way of avoiding competing constraints on an inflow boundary is to add an additional reaction coordinate degree of freedom, solved for to create a set of modified inflow concentrations that fulfill the domain equilibrium condition. The reaction coordinate gives rise to a concentration shift, which is the offset to the inflow concentrations provided by the user. The shift for each species obeys the stoichiometry of the reaction and the equilibrium expression. The modified inflow concentrations are then used in the boundary conditions for the domain mass transport equations. The resulting modified inflow concentrations can be seen as the stationary solution for a batch reactor with the user inflow concentrations as initial concentrations. In addition, the domain reaction rate degree of freedom of the equilibrium reaction is constrained to zero on all Inflow boundaries.

EQUILIBRIUM REACTIONS AND CONCENTRATION BOUNDARY CONDITIONS

No special treatment is made with regards to input concentration values of the Concentration boundary node. Using this feature, you can explicitly set one or a set of concentrations, and the equilibrium condition acts on the rest of the concentrations.

However, there is no solution to the problem if more concentrations than the number of species minus the number of equilibrium reactions are set using this feature.

EQUILIBRIUM REACTIONS AND TIME-DEPENDENT SIMULATIONS

Spurious oscillations may occur in a time-dependent problem if the initial conditions do not fulfill the equilibrium condition. Since equilibrium reactions are assumed to be infinitely fast, the solution is to initialize the problem using an additional study step, solving for a stationary problem with all nonequilibrium reaction rates set to zero. Manual scaling of the reaction rate dependent variables is needed in this study step.

Convective Term Formulation

The default node attributed to The Transport of Diluted Species Interface assumes chemical species transport through diffusion and convection (depending on the modules licensed, a check box to activate migration is available) and implements the mass balance equation in Equation 5-6.

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:

$$\text{nonconservative: } \frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c = \nabla \cdot \mathbf{J}_i + R \qquad (5\text{-}8)$$

$$\text{conservative: } \frac{\partial c}{\partial t} + \nabla \cdot (c\mathbf{u}) = \nabla \cdot \mathbf{J}_i + R \qquad (5\text{-}9)$$

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 5-8 and Equation 5-9 by clearing the Convection check box in the Transport Mechanisms section for The Transport of Diluted Species Interface. The equation then becomes

$$\frac{\partial c}{\partial t} = \nabla \cdot \mathbf{J}_i + R$$

Mass Sources for Species Transport

Note: The features below are only available in a limited set of add-on products. For a detailed overview of which features are available in each product, visit https://www.comsol.com/products/specifications/

There are two types of mass sources in the Transport of Diluted Species interface: point sources and line sources.

POINT SOURCE

A point source is theoretically formed by assuming a mass injection/ejection, $\dot{Q}_c$ (SI unit: mol/(m^3·s)), in a small volume δV and then letting the size of the volume tend to zero while keeping the total mass flux constant. Given a point source strength, $\dot{q}_{p,c}$ (SI unit: mol/s), this can be expressed as

$$\lim_{\delta V \to 0} \int_{\delta V} \dot{Q}_c = \dot{q}_{p,c} \qquad (5\text{-}10)$$

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 5-10, $\dot{Q}_c$ must tend to plus or minus infinity as δV tends to zero. This means that in theory the concentration also tends to plus or minus infinity.

Observe that "point" refers to the physical representation of the source. A point source can therefore only be added to points in 3D components and to points on the symmetry axis in 2D axisymmetry components. Other geometrical points in 2D components represent physical lines.

The finite element representation of Equation 5-10 corresponds to a finite concentration at a point with the effect of the point source spread out over a region around the point. The size of the region depends on the mesh and on the strength of the source. A finer mesh gives a smaller affected region but also a more extreme concentration value. It is important not to mesh too finely around a point source since this can result in unphysical concentration values. It can also have a negative effect on the condition number for the equation system.

LINE SOURCE

A line source can theoretically be formed by assuming a source of strength $\dot{Q}_{l,c}$ (SI unit: mol/(m^3·s)), located within a tube with cross section δS and then letting δS tend to zero while keeping the total mass flux per unit length constant. Given a line source strength, $\dot{q}_{l,c}$ (SI unit: mol/(m·s)), this can be expressed as

$$\lim_{\delta S \to 0} \int_{\delta S} \dot{Q}_{l,c} = \dot{q}_{l,c} \tag{5-11}$$

As in the point source case, an alternative approach is to assume that mass is injected/extracted through the surface of a small object. This results in the same mass source, but requires that effects resulting from the physical object's volume are neglected.

The weak contribution

$$\dot{q}_{l,c} \text{test}(c)$$

is added on lines in 3D or at points in 2D (which represent cut-through views of lines). Line sources can also be added on the axisymmetry line in 2D axisymmetry components. It cannot, however, be added on geometrical lines in 2D since those represent physical planes.

As with a point source, it is important not to mesh too finely around the line source.

For feature node information, see Line Mass Source and Point Mass Source.

Adding Transport Through Migration

Note: Migration is only available in a limited set of add-on products. For a detailed overview of which features are available in each product, visit https://www.comsol.com/products/specifications/

In addition to transport due to convection and diffusion, the Transport of Diluted Species interface supports ionic species transport by *migration*. This is done by selecting the Migration in Electric Field check box under the Transport Mechanisms section for the physics interface. The mass balance then becomes:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (- D_i \nabla c_i - z_i u_{\mathrm{m},i} F c_i \nabla V + c_i \mathbf{u}) \; = \; R_i \qquad (5\text{-}12)$$

where

- c_i (SI unit: mol/ m^3) denotes the concentration of species i
- D_i (SI unit: m^2/s) is the diffusion coefficient of species i
- $\mathbf{u}$ (SI unit: m/s) is the fluid velocity
- F (SI unit: A·s/mol) refers to Faraday's constant
- V (SI unit: V) denotes the electric potential
- z_i (dimensionless) is the charge number of the ionic species, and
- $u_{\mathrm{m},i}$ (SI unit: mol·s/kg) is its ionic mobility

In this case the diffusive flux vector is

$$\mathbf{J}_i \; = \; - D_i \nabla c_i - z_i u_{\mathrm{m},i} F c_i \nabla V$$

The velocity, $\mathbf{u}$, can be a computed fluid velocity field from a Fluid Flow interface or a specified function of the spatial variables x, y, and z. The potential can be provided by an expression or by coupling the system of equations to a current balance, such as the Electrostatics interface. Sometimes it is assumed to be a supporting electrolyte present, which simplifies the transport equations. In that case, the modeled charged species concentration is very low compared to other ions dissolved in the solution. Thus, the species concentration does not influence the solution's conductivity and the net charge within the fluid.

The Nernst-Einstein relation can in many cases be used for relating the species mobility to the species diffusivity according to

$$u_{m,i} = \frac{D_i}{RT}$$

where R (SI unit: J/(mol·K)) is the molar gas constant and T (SI unit: K) is the temperature.

Note: In the *Nernst-Planck Equations* interface, the ionic species contribute to the charge transfer in the solution. It includes an *electroneutrality condition* and also computes the electric potential field in the electrolyte. For more information, see Theory for the Nernst-Planck Equations Interface. This interface is included in the Chemical Reaction Engineering Module.

Supporting Electrolytes

In *electrolyte* solutions, a salt can be added to provide a high electrolyte conductivity and decrease the ohmic losses in a cell. These solutions are often called *supporting electrolytes*, buffer solutions, or carrier electrolytes. The added species, a negative and a positive ion pair, predominates over all other species. Therefore, the supporting electrolyte species can be assumed to dominate the current transport in the solution. In addition, the predominant supporting ions are usually selected so that they do not react at the electrode surfaces since the high conductivity should be kept through the process, that is, they should not be electro-active species. This also means that the concentration gradients of the predominant species in a supporting electrolyte are usually negligible.

Modeling and solving for a supporting electrolyte in the *Electrostatics* or *Secondary Current Distribution* interfaces will give a potential distribution that drives the migration in the Transport of Diluted Species Interface.

The current density vector is proportional to the sum of all species fluxes as expressed by Faraday's law:

$$\mathbf{i} = F\sum_i z_i \mathbf{N}_i$$

The electroneutrality condition ensures that there is always a zero net charge at any position in a dilute solution. Intuitively, this means that it is impossible to create a current by manually pumping positive ions in one direction and negative ions in the other. Therefore, the convective term is canceled out to yield the following expression for the electrolyte current density, where j denotes the supporting species:

$$\mathbf{i} = F\sum_{j} -z_j^2 u_{\mathrm{m},j} F c_j \nabla\phi \tag{5-13}$$

Equation 5-13 is simply Ohm's law for ionic current transport and can be simplified to

$$\mathbf{i} = -\kappa\nabla\phi \tag{5-14}$$

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 5-14, yields:

$$\nabla \cdot (-\kappa\nabla\phi) = 0 \tag{5-15}$$

Equation 5-15 can be easily solved using the Electrostatics or Secondary Current Distribution interface and, when coupled to the Transport in Diluted Species interface, the potential distribution shows up in the migration term.

Crosswind Diffusion

Transport of diluted species applications can often result in models with a very high cell Péclèt number — that is, systems where convection or migration dominates over diffusion. Streamline diffusion and crosswind diffusion are of paramount importance to obtain physically reasonable results. The Transport of Diluted Species interface provides two crosswind diffusion options using different formulations. Observe that crosswind diffusion makes the equation system nonlinear even if the transport equation is linear.

DO CARMO AND GALEÃO

This is the formulation described in Numerical Stabilization in the *COMSOL Multiphysics Reference Manual*. The method reduces over- and undershoots to a minimum, even for anisotropic meshes.

In some cases, the resulting nonlinear equation system can be difficult to converge. This can happen when the cell Péclèt number is very high and the model contains many thin layers, such as contact discontinuities. You then have three options:

• Refine the mesh, especially in regions with thin layers.

• Use a nonlinear solver with a constant damping factor less than one.

• Switch to the Codina crosswind formulation.

CODINA

The Codina formulation is described in Ref. 1. It adds diffusion strictly in the direction orthogonal to the streamline direction. Compared to the do Carmo and Galeão formulation, the Codina formulation adds less diffusion but is not as efficient at reducing over- and undershoots. It also does not work as well for anisotropic meshes. The advantage is that the resulting nonlinear system is easier to converge and that underresolved gradients are less smeared out.

Danckwerts Inflow Boundary Condition

Constraining the composition to fixed values at an inlet to a reactor may sometimes result in issues with unreasonably high reaction rates or singularities at the inlet boundary. These problems may many times be mitigated by using a flux boundary condition instead, based on the upstream concentrations and the fluid velocity at the boundary. In chemical engineering, this type of flux boundary condition is also known as a Danckwerts condition.

Use the Danckwerts condition to specify inlet conditions for domains where high reaction rates are anticipated in the vicinity to the inlet (Ref. 2).

Given an upstream concentration $c_{i,0}$, the Danckwerts inflow boundary condition prescribed the total flux as

$$\mathbf{n} \cdot (\mathbf{J}_i + \mathbf{u}c_i) = \mathbf{n} \cdot (\mathbf{u}c_{i,0}) \tag{5-16}$$

Mass Balance Equation for Transport of Diluted Species in Porous Media

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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:

$$\frac{\partial}{\partial t}(\theta c_i) + \frac{\partial}{\partial t}(\rho c_{P,i}) + \frac{\partial}{\partial t}(a_v c_{G,i}) + \mathbf{u} \cdot \nabla c_i =$$
$$\nabla \cdot [(D_{D,i} + D_{e,i}) \nabla c_i] + R_i + S_i \tag{5-17}$$

On the left-hand side of Equation 5-17, 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 5-17 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; the matrix (drained) density, $\rho = (1 - \varepsilon_p)\rho_p$, and the solid phase density ρ_p.

For saturated porous media, the liquid volume fraction θ is equal to the porosity ε_p, but for partially saturated porous media, they are related by the saturation s as $\theta = s\varepsilon_p$. The resulting gas volume fraction is $a_v = \varepsilon_p - \theta = (1-s)\varepsilon_p$.

On the right-hand side of Equation 5-17, 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 5-17 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

$$\frac{\partial}{\partial t}(\rho c_{P,i}) \;=\; \rho \frac{\partial c_{P,i}}{\partial c_i} \frac{\partial c_i}{\partial t} - \rho c_{P,i} \frac{\partial \varepsilon_P}{\partial t} \;=\; \rho K_{P,i} \frac{\partial c_i}{\partial t} - \rho c_{P,i} \frac{\partial \varepsilon_P}{\partial t} \qquad (5\text{-}18)$$

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

$$\frac{\partial}{\partial t} a_v c_{G,i} \;=\; a_v \frac{\partial c_{G,i}}{\partial c_i} \frac{\partial c_i}{\partial t} + k_{G,i} c_i \frac{\partial a_v}{\partial t} \;=\; a_v k_{G,i} \frac{\partial c_i}{\partial t} + k_{G,i} c_i \frac{\partial a_v}{\partial t} \qquad (5\text{-}19)$$

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, $\theta = \varepsilon_p$, and the governing equations are

$$\frac{\partial}{\partial t}(\varepsilon_p c_i) + \frac{\partial}{\partial t}(\rho c_{P,i}) + \mathbf{u} \cdot \nabla c_i \;=\; \nabla \cdot [(D_{D,i} + D_{e,i}) \nabla c_i] + R_i + S_i \qquad (5\text{-}20)$$

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:

$$\mathbf{u}_a = \frac{\mathbf{u}}{\varepsilon_p} \qquad \text{Saturated}$$

$$\mathbf{u}_a = \frac{\mathbf{u}}{\theta} \qquad \text{Partially saturated}$$

where ε_p is the porosity and $\theta = s\varepsilon_p$ the liquid volume fraction, and s the saturation, a dimensionless number between 0 and 1.
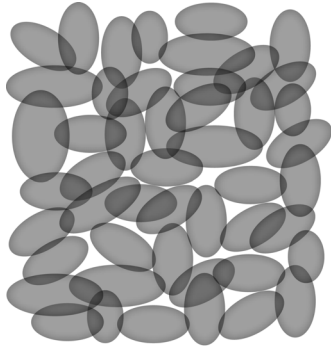
Figure 5-1: A block of a porous medium consisting of solids and the pore space between the solid grains. The average linear velocity describes how fast the fluid moves within the pores. The Darcy velocity attributes this flow over the entire fluid-solid face.

CONVECTIVE TERM FORMULATION

The Transport of Diluted Species in Porous Media interface includes two formulations of the convective term. The conservative formulation of the species equations in Equation 5-17 is written as:

$$\frac{\partial}{\partial t}(\theta c_i) + \frac{\partial}{\partial t}(\rho_b c_{P,i}) + \frac{\partial}{\partial t}(a_v c_{G,i}) + \nabla \cdot \mathbf{u} c_i =$$
$$\nabla \cdot [(D_{D,i} + D_{e,i})\nabla c_i] + R_i + S_i \qquad (5\text{-}21)$$

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 5-17.

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. Depending on the transport of diluted species occurs in free flow, saturated or partially saturated porous media, the effective diffusivity is defined as:

$$D_e = D_F \qquad \text{Free Flow}$$

$$D_e = \frac{\varepsilon_p}{\tau_L} D_L \qquad \text{Saturated Porous Media}$$

$$D_e = \frac{\theta}{\tau_L} D_L \qquad \text{Partially Saturated Porous Media}$$

$$D_e = \frac{\theta}{\tau_L} D_L + \frac{a_v}{\tau_G} k_G D_G \quad \text{Partially Saturated with Volatilization}$$

Here D_F, D_L, and D_G are the single-phase diffusion coefficients for the species diluted in fluid, pure liquid, and gas phases, respectively (SI unit: m^2/s), and τ_F, τ_L, and τ_G are the corresponding tortuosity factors (dimensionless).

The tortuosity factor accounts for the reduced diffusivity due to the fact that the solid grains impede Brownian motion. The interface provides predefined expressions to compute the tortuosity factors in partially saturated porous media according to the Millington and Quirk model (Ref. 12):

$$\tau_L = \theta^{-7/3} \varepsilon^2, \ \tau_G = a_v^{-7/3} \varepsilon^2$$

and Bruggeman model

$$\tau_L = \theta^{-5/2} \varepsilon^2, \ \tau_G = a_v^{-5/2} \varepsilon^2$$

For saturated porous media $\theta = \varepsilon_p$. The fluid tortuosity for the Millington and Quirk model is

$$\tau_L = \varepsilon_p^{-1/3}$$

and for the Bruggeman model the tortuosity is defined as

$$\tau_L = \varepsilon_p^{-1/2}$$

User defined expressions for the tortuosity factor can also be applied.

Dispersion

The contribution of dispersion to the mixing of species typically overshadows the contribution from molecular diffusion, except when the fluid velocity is very small.

The spreading of mass, as species travel through a porous medium is caused by several contributing effects. Local variations in fluid velocity lead to mechanical mixing referred to as dispersion occurs because the fluid in the pore space flows around solid particles, so the velocity field varies within pore channels. The spreading in the direction parallel to the flow, or *longitudinal dispersivity*, typically exceeds the *transverse dispersivity* from up to an order of magnitude. Being driven by the concentration gradient alone, molecular diffusion is small relative to the mechanical dispersion, except at very low fluid velocities.
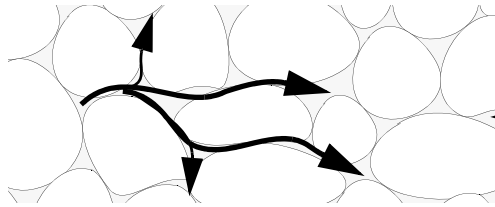
Figure 5-2: Spreading of fluid around solid particles in a porous medium.

 is controlled through the dispersion tensor D_D. The tensor components can either be given by user-defined values or expressions, or derived from the directional dispersivities.

Using the longitudinal and transverse dispersivities in 2D, the dispersivity tensor components are (Ref. 9):

$$D_{\text{D}ii} = \alpha_{\text{L}} \frac{u_i^2}{|\mathbf{u}|} + \alpha_{\text{T}} \frac{u_j^2}{|\mathbf{u}|}$$

$$D_{\text{D}ij} = D_{\text{D}ji} = (\alpha_{\text{L}} - \alpha_{\text{T}}) \frac{u_i u_j}{|\mathbf{u}|}$$

In these equations, $D_{\text{D}ii}$ (SI unit: m^2/s) are the principal components of the dispersivity tensor, and $D_{\text{D}ji}$ and $D_{\text{D}ji}$ are the cross terms. The parameters α_{L} and α_{T} (SI unit: m) specify the longitudinal and transverse dispersivities; and u_i (SI unit: m/s) stands for the velocity field components.

In order to facilitate modeling of stratified porous media in 3D, the tensor formulation by Burnett and Frind (Ref. 10) can be used. Consider a transverse isotropic media, where the strata are piled up in the z direction, the dispersivity tensor components are:

$$
\begin{aligned}
D_{\text{L}xx} &= \alpha_1 \frac{u^2}{|\mathbf{u}|} + \alpha_2 \frac{v^2}{|\mathbf{u}|} + \alpha_3 \frac{w^2}{|\mathbf{u}|} \\
D_{\text{L}yy} &= \alpha_1 \frac{v^2}{|\mathbf{u}|} + \alpha_2 \frac{u^2}{|\mathbf{u}|} + \alpha_3 \frac{w^2}{|\mathbf{u}|} \\
D_{\text{L}zz} &= \alpha_1 \frac{w^2}{|\mathbf{u}|} + \alpha_3 \frac{u^2}{|\mathbf{u}|} + \alpha_3 \frac{v^2}{|\mathbf{u}|} \\
D_{\text{L}xy} &= D_{\text{L}yx} = (\alpha_1 - \alpha_2) \frac{uv}{|\mathbf{u}|} \\
D_{\text{L}xz} &= D_{\text{L}zx} = (\alpha_1 - \alpha_3) \frac{uw}{|\mathbf{u}|} \\
D_{\text{L}yz} &= D_{\text{L}zy} = (\alpha_1 - \alpha_3) \frac{vw}{|\mathbf{u}|}
\end{aligned}
\tag{5-22}
$$

In Equation 5-22 the fluid velocities u, v, and w correspond to the components of the velocity field $\mathbf{u}$ in the x, y, and z directions, respectively, and α_1 (SI unit: m) is the longitudinal dispersivity. If z is the vertical axis, α_2 and α_3 are the dispersivities in the transverse horizontal and transverse vertical directions, respectively (SI unit: m). Setting $\alpha_2 = \alpha_3$ gives the expressions for isotropic media shown in Bear (Ref. 9 and Ref. 11).

Adsorption

As species travel through a porous medium they typically attach to (adsorb), and detach (desorb) from the solid phase, which slows chemical transport through the porous medium. Adsorption and desorption respectively reduces or increases species

concentrations in the fluid. The adsorption properties vary between chemicals, so a plume containing multiple species can separate into components (Ref. 6). The Adsorption feature includes four predefined and one user defined relationships to predict the solid concentrations, c_{Pi} from the concentration in the liquid phase, c_i:

$$c_P = c_{Pmax}\frac{K_L c}{1 + K_L c} \qquad\qquad \text{Langmuir}$$

$$c_P = K_F\left(\frac{c}{c_{ref}}\right)^N \qquad\qquad \text{Freundlich}$$

$$c_P = c_{Pmax}\frac{b_T c}{(1 + (b_T c)^{N_T})^{1/N_T}} \qquad \text{Toth} \qquad\qquad (5\text{-}23)$$

$$c_P = \frac{K_B c_0 c}{(c_S - c)\left(1 + (K_B - 1)\dfrac{c}{c_S}\right)} \qquad \text{BET}$$

The above equations contains the following parameters:

- Freundlich: Freundlich constant K_F (SI unit:·mol/kg), Freundlich exponent N_F (dimensionless), and reference concentration c_{ref} (SI unit: mol/m^3).
- Langmuir: Langmuir constant K_L (SI unit: m^3/mol), and adsorption maximum c_{Pmax} (SI unit: mol/kg).
- Toth: Toth constant b_T (SI unit: m^3/mol), Toth exponent N_T (dimensionless), and adsorption maximum c_{Pmax} (SI unit: mol/kg).
- BET (Braunauer-Emmett-Teller): BET constant K_B (dimensionless), and a monolayer adsorption capacity c_0 (SI unit: mol/kg) and a Saturation concentration, c_S(SI unit: mol/m^3).

These predefined expressions are adsorption isotherms that describe the amount of species sorbed to the solid. Defined at equilibrium, the switch between liquid and solid phases is instantaneous.

Using a Species Source feature, arbitrary expressions can be entered to define, for example, nonequilibrium and temperature-dependent adsorption laws, including those set out by Fetter (Ref. 7) and Bear and Verruijt (Ref. 8).

The retardation factor, RF, describes how adsorption slows the solute velocity, $\mathbf{u}_c$, relative to the average linear velocity of the fluid, $\mathbf{u}_a$, as in

$$\mathrm{RF} \ = \ 1 + \frac{\rho_b}{\theta} \frac{\partial c_P}{\partial c} \ = \ \frac{\mathbf{u}_a}{\mathbf{u}_c}$$

If the contaminant moves at the average linear velocity of the fluid for $\mathrm{RF} = 1$. For $\mathrm{RF} > 1$, the contaminant velocity is smaller than the fluid velocity owing to residence time on solids.

Reactions

Chemical reactions of all types influence species transport in porous media. Examples include biodegradation, radioactive decay, transformation to tracked products, temperature- and pressure-dependent functions, exothermic reactions, and endothermic reactions. The reactions represent change in species concentration per unit volume porous medium per time. Reaction terms are used on the right-hand side of the governing equation to represent these processes. For reactions in a fluid phase, multiply the expression by the fluid volume fraction θ. Similarly, solid phase reaction expressions include the bulk density, ρ_b, and gas phase reactions include the gas volume fraction, a_v.

The following expressions define some common types of reactions:

$$R_{Li} = -\theta \frac{\ln 2}{\lambda_{Li}} c_i \qquad \text{Radioactive decay — liquid}$$

$$R_{Pi} = -\rho_b \frac{\ln 2}{\lambda_{Pi}} \left(\frac{\partial c_{Pi}}{\partial c_i}\right) c_i \quad \text{Radioactive decay — solid}$$

$$R_{Gi} = -\frac{\ln 2}{\lambda_{Gi}} a_v \left(\frac{\partial c_{Gi}}{\partial c}\right) c_i \quad \text{Radioactive decay — gas}$$

$$R_{Lk} = \theta \zeta_{Li} c_i \qquad \text{Creation from parent } c_{Li} \text{ — liquid}$$

$$R_{Pk} = \rho_b \zeta_{Pi} \left(\frac{\partial c_{Pi}}{\partial c_i}\right) c_i \quad \text{Creation from sorbed parent } c_{Pi} \text{ — solid}$$

$$R_{Gk} = -\zeta a_v \left(\frac{\partial c_{Gi}}{\partial c}\right) c_i \quad \text{Reaction — gas}$$

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. 13:

$$\zeta_T \;=\; \zeta_R \exp\!\left[\frac{E_a(T-T_R)}{R_u T T_R}\right] \qquad (5\text{-}24)$$

In Equation 5-24, 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 5-17. The resulting equation is:

$$d_{\mathrm{fr}}\!\left(\frac{\partial \rho_b c_{\mathrm{P},i}}{\partial t} + \frac{\partial \varepsilon_p c_i}{\partial t} + \nabla_t \cdot (D_{\mathrm{e},i}\nabla_t c_i) + \mathbf{u}\cdot\nabla_t c_i\right) \;=\; d_{\mathrm{fr}}R_i + d_{\mathrm{fr}}S_i + n_0 \qquad (5\text{-}25)$$

Here d_{fr} is the fracture thickness, $c_{\mathrm{P},i}$ the amount of species adsorbed to (or desorbed from) the porous matrix (moles per unit dry weight of the solid), ε_p is the fracture porosity, and D_{e} is the effective diffusivity. The first two terms on the right hand side represent source terms from reactions, and n_0 corresponds to out-of plane flux from the adjacent porous domain.

In order to arrive at the tangential differential equation, the gradient is split into the contributions normal and tangential to the fracture:

$$\nabla c_i \;=\; \nabla_n c_i + \nabla_t c_i$$

The normal gradient is defined in the direction normal to the boundary representing the fracture and the tangential gradient is defined along the boundary. Assuming that the variations in the normal (thin) direction of the fracture are negligible compared to those in the tangential direction, the gradient is simplified as:

$$\nabla c_i = \nabla_t c_i$$

Using The Transport of Diluted Species in Fractures Interface, the transport along fracture boundaries alone is solved for. In this case the transport in the surrounding porous media neglected and the out-of plane flux n_0 vanishes.

See Fracture for more information about the boundary feature solving Equation 5-25. See The Transport of Diluted Species in Fractures Interface for more information about the physics interface solving the equation on boundaries only.

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Theory for the Electrophoretic Transport Interface

The Electrophoretic Transport Interface models transport of charged and uncharged species, and in addition sets up a charge balance equation for the electrolyte potential.

The species concentrations are denoted, c_i (SI unit: mol/m^3), and the potential, ϕ_l (SI unit: V).

The species are transported by diffusion, migration, and (optionally) convection according the Nernst-Planck set of equations. The total flux of species i is denoted $\mathbf{N}_i$ (SI unit: mol/(m^2·s)) according to

$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_l + \mathbf{u} c_i = \mathbf{J}_i + \mathbf{u} c_i \qquad (5\text{-}26)$$

where D_i (SI unit: m^2/s) is the diffusion coefficient, z_i (1) the corresponding charge, $u_{m,i}$ (SI unit: s·mol/kg) the mobility and $\mathbf{u}$ (SI unit: m/s) the velocity vector. $\mathbf{J}_i$ denotes the molar flux relative to the convective transport (SI unit: mol/(m^2·s)). For a detailed description of the theory of these equations and the different boundary conditions, see Theory for the Transport of Diluted Species Interface.

CHARGE BALANCE EQUATION

The current vector, $\mathbf{i}_l$ (A/m^2), is defined as

$$\mathbf{i}_l = \sum_i z_i \mathbf{N}_i \qquad (5\text{-}27)$$

where the summation is made over all species in the electrolyte.

The governing equation for the electrolyte potential is

$$\nabla \cdot \mathbf{i}_l = Q_l \qquad (5\text{-}28)$$

where Q_l (SI unit: A/m^3) is the electrolyte current source stemming from, for example, porous electrode reactions. For non-porous electrode domains this source term is usually zero.

PROTON AND HYDROXIDE CONCENTRATIONS AND ELECTRONEUTRALITY

Assuming the total number of species to be $N+2$, the assumption of electroneutrality is

$$\sum_{i=1}^{N+2} z_i c_i = 0 \tag{5-29}$$

In water-based systems the species H+ and OH- are always present. The auto ionization reaction for water is

$$H_2O \leftrightarrow H^+ + OH^- \tag{5-30}$$
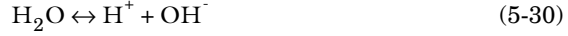
This reaction is fast, following the equilibrium relation

$$c_{H^+} c_{OH^-} = K_w \times 1 \text{ mol}^2 \text{dm}^{-6} \tag{5-31}$$

where $K_w \approx 10^{-14}$.

Now, the electroneutrality condition, including the two additional species H+ and OH-, reads

$$c_{H^+} - c_{OH^-} + \sum_{i=1}^{N} z_i c_i = 0 \tag{5-32}$$

Combining these two equations results in the following algebraic expressions for the concentrations of H+ and OH-.

$$c_{H^+} = -\frac{\Sigma}{2} + \sqrt{\frac{\Sigma^2}{4} + K_w \times 1 \text{ mol}^2 \text{dm}^{-6}} \tag{5-33}$$

and

$$c_{OH^-} = \frac{\Sigma}{2} + \sqrt{\frac{\Sigma^2}{4} + K_w \times 1 \text{ mol}^2 \text{dm}^{-6}} \tag{5-34}$$

where

$$\Sigma = \sum_{i=1}^{N} z_i c_i \tag{5-35}$$

MASS BALANCE EQUATIONS FOR DISSOCIATION SPECIES

Assume a set of species Si describing k dissociation steps from

$$S_k^{z_0+k} \leftrightarrow S_{k-1}^{z_0+k-1} + H^+ \qquad K_{a,1} = \frac{[H^+][S_{k-1}^{z_0+k-1}]}{[S_k^{z_0+k}]} \qquad (5\text{-}36)$$

to

$$S_k^{z_0+1} \leftrightarrow S_0^{z_0} + H^+ \qquad K_{a,k} = \frac{[H^+][S_0^{z_0}]}{[S_1^{z_0+1}]} \qquad (5\text{-}37)$$

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 represents the species activity. The charge of each species is always deductible from the index i according to z_{0+i} and will be dropped from now on.

If the proton activity is known, any species S_m may be expressed using any other species S_l according to

$$[S_m] = \frac{[H]^{m-l}[S_l]}{\displaystyle\prod_{j=k-m+1}^{k-l} K_{a,j}} \qquad (5\text{-}38)$$

if $m>l$ and

$$[S_m] = [H]^{m-l}[S_l] \prod_{j=k-l+1}^{k-m} K_{a,j} \qquad (5\text{-}39)$$

if $l>m$.

Setting $m=i$ and denoting the flux of species i by $\mathbf{N}_i$ using equation Equation 5-26, the mass balance equation for the concentration c_i of each subspecies i in the dissociation chain is

$$\frac{\delta c_i}{\delta t} + \nabla \cdot \mathbf{N}_i = R_{eq,i,k-i} - R_{eq,i,k-i+1} + R_i \qquad (5\text{-}40)$$

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

$$\sum_{i=0}^{k} \left(\frac{\delta c_i}{\delta t} + \nabla \cdot \mathbf{N}_i \right) = \sum_{i=0}^{k} R_i \qquad (5\text{-}41)$$

AVERAGE IONIZATION FORMULATION FOR LARGE MOLECULES

Large protein molecules are typically subject to a large number of dissociation steps.

As an alternative way to a long chain of dissociation steps for describing protein transport, one can instead formulate the protein transport based on the average number of protons $\bar{\nu}$ (1) removed from the molecule. $\bar{\nu}$ is typically provided as a function of pH, based on experimental data. The average charge of the species then is $\bar{z} = z_0 - \bar{\nu}$, so that the flux of the species is written as:

$$\mathbf{N}_i = -D\nabla c_i - \bar{z} u_m F c_i \nabla \phi_l + \mathbf{u} c_i \qquad (5\text{-}42)$$

and similarly the addition to the charge neutrality condition is $\bar{z} c_i$.

When considering the contribution to the current and the charge balance equation one needs to take into account that the squared average charge, $\bar{z}^2 = (z_0 - \bar{\nu})^2$, is not equal to the "average squared charge", $\overline{z^2} = z_0^2 + 2z_0\bar{\nu} + \overline{\nu^2} = \bar{z}^2 - \bar{\nu}^2 + \overline{\nu^2}$ (Ref. 1).

The addition to the current density vector is

$$\mathbf{i}_l = \dots - F(\bar{z} D_i \nabla c_i + \overline{z^2} u_m c_i \nabla \phi_l) \qquad (5\text{-}43)$$

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

$$\overline{\nu^2} = -c_{H^+} \frac{d}{dc_{H^+}} \bar{\nu} + \bar{\nu}^2 \qquad (5\text{-}44)$$

And from this one can derive the average squared charge according to

$$\overline{z^2} = -c_{H^+} \frac{d}{dc_{H^+}} \bar{\nu} + \bar{z}^2 = -c_{H^+} \frac{d}{dc_{H^+}} \bar{z} + \bar{z}^2 \qquad (5\text{-}45)$$

DIFFUSIVITY-MOBILITY RELATIONS

The Stokes radius r of a molecule is related to the diffusivity according to

$$r = \frac{kT}{6\pi\mu D} \qquad (5\text{-}46)$$

where is the μ (SI unit: Pa·s) is the dynamic viscosity and k the Boltzmann constant.

For small molecules, one frequently uses the Nernst-Einstein relation between the diffusivity and the mobility

$$u_m = \frac{D}{RT} \tag{5-47}$$

For larger molecules, such as proteins, the mobility may instead be calculated based on the Debye-Hückel-Henry expression (Ref. 2) according to

$$u_m = \frac{ef(\kappa r)}{6\pi\mu F(1 + \kappa r)} = \frac{Df(\kappa r)}{RT(1 + \kappa r)} \tag{5-48}$$

where κ (1/m) is the Debye parameter, which depends on the ionic strength of the solution, is defined for ideal solutions as

$$\kappa^2 = \frac{2e^2 N_A}{\varepsilon\varepsilon_0 kT} \sum_{i=1}^{N} z_i^2 c_i \tag{5-49}$$

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

$$\kappa^2 = \frac{2e^2 N_A}{\varepsilon\varepsilon_0 kT} \left(\sum_{i=1}^{N-M} z_i^2 c_i + \sum_{i=N-M+1}^{N} \text{abs}(z_i)c_i \right) \tag{5-50}$$

REFERENCES

1 *The Dynamics of Electrophoresis*, Mosher, Saville and Thormann, VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1992.

2 *Computer Simulation and Experimental Validation of the Electrophoretic Behavior of Proteins. 2. Model Improvement and Application to Isotachophoresis,* Mosher, Gebauer, Caslavska, and Thormann. *Analytical Chemistry*, Vol. 64, pp. 2991–2997, 1992.

Theory for the Surface Reactions Interface

The Surface Reactions Interface solves for an arbitrary number of surface concentrations, $c_{s,i}$ (SI unit: mol/m^2), referring to species adsorbed on a reactive surface, and an arbitrary number of bulk concentrations $c_{b,k}$ (SI unit: mol/m^3), referring to the species in the solid material that constitutes the bulk of the reactive surface.

In this section:

- Governing Equations for the Surface Concentrations
- Governing Equations for the Bulk Concentrations
- ODE Formulations for Surface Concentrations
- Surface Reaction Equations on Deforming Geometries
- Reference for the Surface Reactions Interface

Governing Equations for the Surface Concentrations

Transport of adsorbed species occurs in the tangential direction along the surface. The Surface Reactions interface models the tangential flux in the surface dimension, the *surface molar flux*, $\mathbf{N}_{t,i}$ (SI unit: mol/(m·s)) (the subscript t refers to the tangential direction), as governed by diffusion according to Fick's law:

$$\mathbf{N}_{t,i} = -D_{s,i}\nabla_t c_{s,i}$$

where $D_{s,i}$ (SI unit: m^2/s) is the surface diffusion coefficient for species i.

The governing equation for the surface concentrations is written as:

$$\frac{\partial c_{s,i}}{\partial t} = -\nabla_t \cdot \mathbf{N}_{t,i} + R_{s,i} \tag{5-51}$$

where $R_{s,i}$ (SI unit: mol/(m^2·s)) is the sum of all sources due to surface reactions and adsorption/desorption phenomena.

Of frequent interest for surface reaction kinetics are the fractional surface coverages, θ_i (dimensionless), of the species (with index i).

Writing the density of sites of the surface as Γ_s (SI unit: mol/m^2) and the site occupancy number for each species as σ_i (dimensionless), the surface coverages can be calculated from:

$$\theta_i = \frac{\sigma_i c_{s,i}}{\Gamma_s}$$

(The site occupancy number accounts for the situation when a large species covers more than one site on the surface.)

For the case of monolayer adsorption, the sum of all fractional coverages of free and adsorbed sites is unity, and hence the fraction of free sites on the surface, θ_*, can be calculated from:

$$\theta_* = 1 - \sum_i \theta_i$$

Governing Equations for the Bulk Concentrations

BULK SPECIES RATES AND GROWTH VELOCITY

The reaction rate for a bulk species of index k, being added to the bulk due to surface reactions is defined as $R_{b,k}$ (SI unit: mol/(s·m^2)).

The reaction rate in mass basis, $r_{b,k}$ (SI unit: kg/(s·m^2)) for species k, is given by:

$$r_k = M_k R_{b,k}$$

with M_k (SI unit: kg/mol) being the molar mass of the species.

Based on this, the species contribution to the bulk growth velocity, v_k (SI unit: m/s), is given by:

$$v_{b,k} = \frac{r_{b,k}}{\rho_k}$$

where ρ_k is the species density (SI unit: kg/m^3).

TOTAL RATES AND VELOCITY

To get the corresponding total values, a summation for all bulk species is made according to:

$$R_{b,\,\text{tot}} = \sum_k R_{b,\,k}$$

$$r_{b,\,\text{tot}} = \sum_k r_{b,\,k}$$

$$v_{b,\,\text{tot}} = \sum_k v_{b,\,k}$$

FRACTIONAL RATES AND VELOCITY

The fractional deposition rates are calculated by:

$$R_{b,\,\text{frac},\,k} = \frac{R_{b,\,k}}{R_{b,\,\text{tot}}}$$

$$r_{b,\,\text{frac},\,k} = \frac{r_{b,\,k}}{r_{b,\,\text{tot}}}$$

$$v_{b,\,\text{frac},\,k} = \frac{v_{b,\,k}}{v_{b,\,\text{tot}}}$$

	The fractional deposition rates can be used as measures of the local fractional composition in a deposited layer at a certain thickness or time.

ACCUMULATED BULK QUANTITIES

By solving for the bulk species concentrations for each time step, the accumulated mass and thickness changes of the bulk material can be calculated.

The bulk concentration, $c_{b,k}$ (SI unit: mol/m^2), for species k is governed by the equation:

$$\frac{\partial c_{b,\,k}}{\partial t} = R_{b,\,k} \tag{5-52}$$

The bulk concentration in mass basis, $m_{b,k}$ (SI unit: kg/m^2) for a species k, can be derived from:

$$m_{b,\,k} = M_k c_{b,\,k}$$

leading to the bulk thickness $s_{b,k}$ (SI unit: m) of species k according to:

$$s_{b,k} = \frac{m_{b,k}}{\rho_k}$$

TOTAL BULK QUANTITIES

The total bulk concentration is calculated according to:

$$c_{b,\text{tot}} = \sum_k c_{b,k}$$

The deposited total mass, $m_{b,\text{tot}}$ (SI unit: kg/m^2) is

$$m_{b,\text{tot}} = \sum_k m_{b,k}$$

and the total bulk thickness, s_{tot} (SI unit: m) is

$$s_{b,\text{tot}} = \sum_k s_k$$

FRACTIONAL QUANTITIES

The fractional bulk concentration, bulk mass, and thickness (all dimensionless) are calculated according to:

$$c_{b,\text{frac},k} = \frac{c_{b,k}}{c_{b,\text{tot}}}$$

$$m_{b,\text{frac},k} = \frac{m_{b,k}}{m_{b,\text{tot}}}$$

$$s_{b,\text{frac},k} = \frac{s_{b,k}}{s_{b,\text{tot}}}$$

ODE Formulations for Surface Concentrations

The surface of a 1D geometry has a 0 dimension, hence no surface transport can be modeled and the governing equation is reduced to an ODE:

$$\frac{\partial c_{s,i}}{\partial t} = R_{s,i}$$

Surface Reaction Equations on Deforming Geometries

If a Surface Reaction interface is used in conjunction with a Deformed Geometry or a Moving Mesh (ale) interface, the boundary concentration can either be assumed to be transported with the deforming geometry (moving mesh), with no compensation for the stretching (the Compensate for boundary stretching check box is not selected), or the species can be assumed to "float" on the mesh (the Compensate for boundary stretching check box is selected, which is the default). In the latter case the following is assumed in regard to the coupling between the surface species and bulk species and the mesh movement:

- Expansion or contraction of the boundary dilutes or increases concentration of the species, respectively, so that the surface integral (in spatial coordinates) of the species is kept constant.

- Tangential mesh movement has no impact on the local concentration in spatial coordinates, that is, the tangential transport of surface and bulk species does not move with the mesh in the tangential direction.

In order to comply with the additional contributions to the mass balance, equations are added. First, the following terms are added to the right-hand side of Equation 5-51 and Equation 5-52, 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 5-51 and Equation 5-52, respectively:

$$\nabla_t \cdot (c_{s,i}\mathbf{v}_{t,\,\text{mesh}})$$

$$\nabla_t \cdot (c_{b,k}\mathbf{v}_{t,\,\text{mesh}})$$

where $\mathbf{v}_{t,\mathrm{mesh}}$ 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
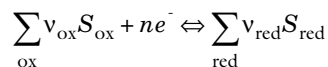
$$\sum_{\text{ox}} v_{\text{ox}} S_{\text{ox}} + ne^- \Leftrightarrow \sum_{\text{red}} v_{\text{red}} S_{\text{red}}$$

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:

$$R_{i,\,\text{molar}} = -\sum_m a_{v,\,m} \frac{v_{i,\,m} i_m}{n_m F}$$

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: $kg/(m^2 \cdot s)$), 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.

6

Fluid Flow Interfaces

This chapter describes the physics interfaces found under the **Fluid Flow** branch (≈). The chapter summarizes each physics interface including the different fields, material properties, and boundary conditions associated with them, and suggests how and when to apply it. In this chapter:

- The Laminar Flow and Creeping Flow Interfaces
- The Brinkman Equations Interface
- The Darcy's Law Interface
- The Free and Porous Media Flow Interface
- Theory for the Laminar Flow and Creeping Flow Interfaces
- Theory for the Brinkman Equations Interface
- Theory for the Darcy's Law Interface
- Theory for the Free and Porous Media Flow 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
- Domain, Boundary, Pair, and Point Nodes for Single-Phase Flow

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🔍	• Theory for the Laminar Flow and Creeping Flow Interfaces

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.

By default, the **Neglect inertial term (Stokes flow)** check box is selected. If unchecked, the inertial terms are included in the computations.

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. $Ma < 0.3$ 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.

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 approximate the time-scale tensor in time dependent problems from projections of weak expressions. This check box is selected by default. When not selected the actual time-step is used.

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.

Q
- Pseudo Time Stepping for Laminar Flow Models
- Domain, Boundary, Pair, and Point Nodes for Single-Phase Flow
- Theory for the Laminar Flow and Creeping Flow Interfaces

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
- Initial Values
- Inlet
- Line Mass Source[1]
- Open Boundary
- Outlet

- Periodic Flow Condition
- Point Mass Source[1]
- 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.

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** (📝) 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/or 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 **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 or expressions should be specified for the **Velocity field u** and the **Pressure *p***.

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
- 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 $\mathbf{u} = 0$.

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.

Navier Slip
This boundary condition enforces no-penetration at the wall, $\mathbf{u} \cdot \mathbf{n}_{\text{wall}} = 0$, and adds a friction force of the form

$$\mathbf{F}_{\text{fr}} = -\frac{\mu}{\beta}\mathbf{u}_{\tan g}$$

where β is a slip length, and $\mathbf{u}_{\tan g} = \mathbf{u} - (\mathbf{u} \cdot \mathbf{n}_{\text{wall}})\mathbf{n}_{\text{wall}}$ 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.

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. Select **User defined** from **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 $\mathbf{u}_{tang}$ 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.

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.

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 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** $\mathbf{u}_\mathrm{w}$ 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 **Default**, **Use pointwise constraints**, **Use DG constraints**, or **Use weak constraints**. **Use 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 **Use DG constraints** is selected.

- Select **Elemental** (default) or **Nodal** under **Constraint method**. This setting is not available for **Use DG constraints** or **Use weak constraints**.

🔍	• Theory for the Wall Boundary Condition
	• The Moving Mesh Interface

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** 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. If 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.

- The **Suppress backflow** option adjusts the inlet pressure locally in order to prevent fluid from 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)**.

Mass Flow Rate

The **Mass flow rate** option sets the integrated mass flow across the entire boundary, 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.

Standard Flow Rate (SCCM)

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.

The **Fully developed flow** option adds contributions to the inflow boundary, which force the flow towards 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}. Observe that P_{av} is the average pressure on the inflow boundary.

The fully developed flow condition requires any volume force to be approximately aligned with the normal of the inlet boundary. A fully developed flow boundary cannot be adjacent to any Interior Wall feature.

CONSTRAINT SETTINGS

This section is displayed by clicking the **Show** button (👁) and selecting **Advanced Physics Options**.

| | • Prescribing Inlet and Outlet Conditions |
| ⓠ | • Normal Stress Boundary Condition |

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** 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. If 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.

- 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 prevent fluid from 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 fully developed flow condition requires any volume force to be approximately aligned with the normal of the outlet boundary. A fully developed flow boundary cannot be adjacent to any Interior Wall feature.

This section is displayed by clicking the **Show** button ( ) and selecting **Advanced Physics Options**.

ⓠ | Prescribing Inlet and Outlet Conditions

Symmetry

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:

$$\mathbf{u} \cdot \mathbf{n} = \mathbf{0}, \qquad \left(-p\mathbf{I} + \left(\mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right)\right)\mathbf{n} = \mathbf{0}$$

$$\mathbf{u} \cdot \mathbf{n} = \mathbf{0}, \qquad (-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T))\mathbf{n} = \mathbf{0}$$

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:

$$\mathbf{u} \cdot \mathbf{n} = \mathbf{0}, \qquad \mathbf{K} - (\mathbf{K} \cdot \mathbf{n})\mathbf{n} = \mathbf{0}$$
$$\mathbf{K} = \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T)\mathbf{n}$$

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 $p \approx f_0$.

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 $p \approx f_0$.

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. 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.

PRESSURE DIFFERENCE

This section is available when **Incompressible flow** is selected for **Compressibility** under the **Physical Model** section for the physics interface.

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** 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** 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*.

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.

A Wall subnode is added by default and it applies to the parts of the pair boundaries where a source boundary lacks a corresponding destination boundary and vice versa. The **Wall** feature can be overridden by any other boundary condition that applies to exterior boundaries. By right-clicking the **Flow Continuity** node, additional Fallback feature subnodes can be added.

The **Wall** fallback condition is incompatible with the **Low Re** wall treatment for the k-ω, SST, and Low Reynolds number k-ε turbulence models.

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. Or, if the reference pressure p_{ref} defined at the physics interface level is equal to zero, p_0 represents the absolute pressure.

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.

Point Mass Source

This feature requires at least one of the following licenses: Batteries & Fuel Cells Module, CFD Module, Chemical Reaction Engineering Module, Corrosion Module, Electrochemistry Module, Electrodeposition 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 Batteries & Fuel Cells 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**, $\dot{q}_{\mathrm{P}}$ 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: Batteries & Fuel Cells Module, CFD Module, Chemical Reaction Engineering Module, Corrosion Module, Electrochemistry Module, Electrodeposition 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 Batteries & Fuel Cells Module, there are two nodes, one for the fluid flow (**Fluid Line Source**) and one for the species (**Species Line Source**).

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 axis of symmetry
3D	Edges

SOURCE STRENGTH

The source **Mass flux**, $\dot{q}_1$, 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.

    🔍   Mass Sources for Fluid Flow in the *COMSOL Multiphysics Reference Manual*

Gravity

This feature requires at least one of the following licenses: CFD Module, Heat Transfer Module.

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**, an edit field for the **Turbulent Schmidt number** appears. See also Theory for Buoyancy-Induced Turbulence in the *CFD Module User's Guide*.

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 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 Fluid and Matrix Properties feature, which adds the Brinkman equations and provides an interface 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** — **Fluid and Matrix Properties**, **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**, and **Inconsistent Stabilization**, and **Advanced Settings** sections, 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.

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, select **Compressible flow (Ma<0.3)** from the **Compressibility** list if there are small variations in the density, typically dependent on the temperature (nonisothermal flow). For compressible flow modeled with the Brinkman Equations interface, the Mach number must be below 0.3.

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.

Enable porous media domains

The **Enable porous media domains** check box is selected by default to solve Brinkman equations in porous domains.

Reference Pressure Level

Enter a **Reference pressure level** p_{ref} (SI unit: Pa). The default value is 1[atm].

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).

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 • Discontinuous Galerkin Formulation

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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:

- Fluid and Matrix Properties
- 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.

Fluid and Matrix Properties

The **Fluid and Matrix Properties** node adds the Brinkman equations: Equation 6-35 and Equation 6-36 (excluding any mass sources), and provides an interface for defining the properties of the fluid material and the porous matrix.

FLUID PROPERTIES

The default **Fluid material** uses the **Domain material**. Select another material as needed.

Both the default **Density** ρ (SI unit: kg/m^3) and **Dynamic viscosity** μ (SI unit: Pa·s) use values **From material** based on the **Fluid material** selection. For **User defined** enter another value or expression. In this case, the default is 0 kg/m^3 for the density and 0 Pa·s for the dynamic viscosity. 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. Non-Newtonian fluids have a viscosity that is shear-rate dependent. Examples of non-Newtonian fluids include yogurt, paper pulp, and polymer suspensions.

POROUS MATRIX PROPERTIES

The default **Porous material** uses the **Domain material** for the porous matrix. Select another material as needed.

The **Porosity** ε_p (a dimensionless number between 0 and 1) uses by default the value **From material** as defined by the **Porous material** selection. For **User defined** the default is 0.

Select a **Permeability model** to specify the capacity of the porous material to transmit flow — **Permeability** to directly enter the permeability of the porous matrix, **Kozeny-Carman** to define the permeability from the porosity and mean particle diameter, or **Non-Darcian** in cases when Darcy's linear relation between pressure drop and velocity is no longer valid due to turbulence or inertial effects. The **Non-Darcian Flow** option includes different models, some of them are only available for certain modules. For a detailed overview of the functionality available in each product, visit http://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**, **Symmetric**, or **Full** to define a tensor value and enter another value or expression in the field or matrix.

For **Kozeny-Carman**, enter the mean **Particle diameter** d_p (SI unit: m), the default value is 0.5 mm.

For **Non-Darcian**, choose a **Non-Darcian flow model** from the selection list. The available options, depending on the modules licensed, are **Forchheimer** or **Ergun**.

For **Forchheimer**, the default **Permeability** κ (SI unit: m^2) uses the value **From material**, as defined by the **Porous material** list. 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 6-46.

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 6-35. 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.

$$\frac{\partial}{\partial t}(\varepsilon_p \rho) + \nabla \cdot (\rho \mathbf{u}) = Q_m \tag{6-3}$$

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 $\mathbf{F}$ on the right-hand side of Equation 6-36. It then acts on each fluid element in the specified domains. A common application is to include gravity effects.

$$\frac{\rho}{\varepsilon_p}\left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\frac{\mathbf{u}}{\varepsilon_p}\right) =$$

$$-\nabla p + \nabla \cdot \left[\frac{1}{\varepsilon_p}\left\{\mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right\}\right] - \left(\kappa^{-1}\mu + \frac{Q_m}{\varepsilon_p^2}\right)\mathbf{u} + \mathbf{F} \tag{6-4}$$

VOLUME FORCE
Enter the components of **Volume force** $\mathbf{F}$ (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.

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 $p + p_{\text{ref}}$ 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.

The Darcy's Law Interface

The **Darcy's Law (dl)** interface (![icon]), found under the **Porous Media and Subsurface Flow** branch (![icon]) 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 Fluid and Matrix Properties node, which provides an interface for defining the fluid material along with the porous medium properties.

When this physics interface is added, the following default nodes are also added in the **Model Builder** — **Fluid and Matrix Properties**, **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

This feature requires a specific license. For a detailed overview of the functionality available in each product visit http://www.comsol.com/products/specifications/.

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 http://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 post processing 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.*

DEPENDENT VARIABLES

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.

Q

- 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 **Batteries_and_Fuel_Cells_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/Flow_and_Solid_Deformation/ 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).

- Fluid and Matrix Properties
- Gravity
- Initial Values
- Storage Model
- Mass Source
- Poroelastic Storage
- Porous Electrode Coupling
- Richards' Equation Model

Note that some features are only available with certain COMSOL products (see http://www.comsol.com/products/specifications/).

BOUNDARY, EDGE, AND POINT

The following nodes (listed in alphabetical order) are available on exterior boundaries:

- Atmosphere/Gauge
- Cross Section
- Electrode-Electrolyte Interface Coupling
- Flux Discontinuity
- Fracture Flow
- 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
- Thickness
- Thin Barrier

[1] This node is described for the Transport of Diluted Species Interface

Note that some features are only available with certain COMSOL products (see http://www.comsol.com/products/specifications/)!

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 Flow
- Thin Barrier

💡	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.

Fluid and Matrix Properties

The **Fluid and Matrix Properties** node adds the equations for Darcy's law, Equation 6-5 and Equation 6-6 (excluding any mass sources), and contains settings for the fluid properties and the porous matrix properties such as the effective porosity.

$$\frac{\partial}{\partial t}(\rho\varepsilon) + \nabla \cdot (\rho\mathbf{u}) \ = \ Q_{\mathrm{m}} \tag{6-5}$$

$$\mathbf{u} = -\frac{\kappa}{\mu}(\nabla p + \rho g \nabla D) \qquad (6\text{-}6)$$

Note that D is the elevation which is only included in the Subsurface Flow Module. Otherwise, D is zero and Equation 6-6 simplifies to:

$$\mathbf{u} = -\frac{\kappa}{\mu}\nabla p \qquad (6\text{-}7)$$

FLUID PROPERTIES

Select the **Fluid material** to use for the fluid properties. Select **Domain material** (the default) to use the material defined for the domain. Select another material to use that material's properties for the fluid.

Density

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.

- 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.

Dynamic Viscosity

Select a **Dynamic viscosity** μ (SI unit: Pa·s). The default uses values **From material** as defined by the **Fluid material** selected. For **User defined** the default is 0 Pa·s.

If the settings for the dynamic viscosity are unavailable, this is due to **Hydraulic conductivity** being selected as the **Permeability model** under the **Matrix Properties** section below. The hydraulic conductivity is defined using a combination of fluid and matrix properties and replaces the need to define the dynamic viscosity. Note that this option is only available with the Subsurface Flow Module.

MATRIX PROPERTIES

Select the material to use as porous matrix. Select **Domain material** from the **Porous material** list (the default) to use the material defined for the porous domain. 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.

Select a **Permeability model** to specify the capacity of the porous material to transmit flow — **Permeability** to define the permeability of the porous matrix, **Hydraulic conductivity** to define a combination of fluid permeability and dynamic viscosity, **Kozeny-Carman** to define the permeability from the porosity and mean particle diameter, or **Non-Darcian** in cases when Darcy's linear relation between pressure drop and velocity is no longer valid due to turbulence or inertial effects.

Note that the option to choose **Hydraulic conductivity** is only available for the Subsurface Flow Module. The **Non-Darcian Flow** option is only available in some modules. For a detailed overview of the functionality available in each product, visit http://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**, **Symmetric**, or **Full** to define a tensor value and enter another value or expression in the field or matrix.

For **Hydraulic conductivity** K (SI unit: m/s) select **Isotropic** to define a scalar value or **Diagonal**, **Symmetric**, or **Full** to define a tensor value. The default is $2.94 \cdot 10^{-4}$ m/s.

For **Kozeny-Carman**, enter the mean **Particle diameter** d_p (SI unit: m), the default value is 0.5 mm.

For **Non-Darcian**, choose a **Non-Darcian flow model** from the selection list. The available options, depending on the modules licensed, are **Forchheimer**, **Ergun**, **Burke-Plummer**, and **Klinkenberg**.

For **Forchheimer**, the default **Permeability** κ (SI unit: m^2) uses the value **From material**, as defined by the **Porous material** list. 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 6-46.

For **Burke-Plummer**, specify the mean **Particle diameter** d_p (default value: 0.5 mm).

If **Klinkenberg** is selected from the list, the default **Permeability** κ_∞ (SI unit: m^2) uses the value **From material**, as defined by the **Porous material** list. Enter the **Klinkenberg parameter** b_K. Its default value is 1e3 Pa. The corrected permeability κ is then calculated using Equation 6-53.

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 6-8, the equation for porosity).

$$\frac{\partial}{\partial t}(\rho\varepsilon) + \nabla \cdot (\rho\mathbf{u}) \;=\; Q_m \qquad (6\text{-}8)$$

For the Fracture Flow Interface — which is available for the Subsurface Flow Module and the Porous Media Flow Module — the mass source is applicable to the right-hand side of Equation 6-11 (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 $0\ kg/(m^3 \cdot s)$.

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.

Storage Model

The **Storage Model** node adds Equation 6-6 and Equation 6-41 (excluding any mass sources). Use it to define the fluid and porous media properties, including a storage term for the specific storage.

This feature requires a specific license. For a detailed overview of the functionality available in each product visit http://www.comsol.com/products/specifications/.

FLUID PROPERTIES

The settings are the same as for the Fluid and Matrix Properties node except a gas constant type is not required.

MATRIX PROPERTIES

The settings are the same as in the Matrix Properties section under Fluid and Matrix Properties.

STORAGE MODEL

Select a **Storage** S (SI unit: 1/Pa) — **Linearized storage** (the default) or **User defined**.

- For **User defined** enter a value or expression for **Storage** S (SI unit: 1/Pa) (S_f in Equation 6-11).

- For **Linearized storage** it uses the following linear equation to define the storage:

$$ S = \varepsilon \chi_f + (1 - \varepsilon_p) \chi_p $$

This is equivalent to the Reuss average of the fluid and solid compressibilities. Enter the value or expression for each of the following:

  - **Compressibility of fluid** χ_f (SI unit: 1/Pa). The default uses values **From material**. For **User defined**, the default is $4 \cdot 10^{-10}$ 1/Pa.
  - **Effective compressibility of matrix** χ_p (SI unit: 1/Pa). The default is $1 \cdot 10^{-4}$ 1/Pa.

FRACTURE FLOW

For the Fracture Flow Interface, enter a value or expression for the **Fracture thickness** d_f (SI unit: m). The default is 0.1 m.

▦	*Discrete Fracture*: Application Library path **Subsurface_Flow_Module/ Fluid_Flow/discrete_fracture**

Richards' Equation Model

The **Richards' Equation Model** node defines the storage and retention models in variably saturated porous media. See the Richards' Equation Model described for the Richards' Equation interface.

This feature requires a specific license. For a detailed overview of the functionality available in each product visit http://www.comsol.com/products/specifications/.

Poroelastic Storage

The **Poroelastic Storage** node adds Equation 6-6 and Equation 6-41 (excluding any mass sources). Use it to define the fluid and porous media properties, including a storage term to account for the Poroelasticity multiphysics coupling.

This feature requires a specific license. For a detailed overview of the functionality available in each product visit http://www.comsol.com/products/specifications/.

FLUID PROPERTIES

The settings are the same as for the Storage Model node except a gas constant type is not required. There is also an option to define the fluid compressibility.

Compressibility

Select the **Compressibility of fluid** χ_f (SI unit: 1/Pa). The default uses values **From material** as defined by the **Fluid material** selected. For **User defined** the default is $4 \cdot 10^{-10}$ 1/Pa.

MATRIX PROPERTIES

The settings are the same as in the Matrix Properties section under Fluid and Matrix Properties.

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.

This feature requires a specific license. For a detailed overview of the functionality available in each product visit http://www.comsol.com/products/specifications/.

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). Select the check box **Specify reference position** to define a reference elevation.

Select the acceleration of gravity from either the Darcy's Law interface Settings (default), or specify a user defined value. When the check box **Include gravity** is not selected in the Darcy's Law interface Settings, the elevation *D* is set equal to zero.

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.

This feature requires a specific license. For a detailed overview of the functionality available in each product visit http://www.comsol.com/products/specifications/.

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.

This feature requires a specific license. For a detailed overview of the functionality available in each product visit http://www.comsol.com/products/specifications/.

SPECIES

Based on the number of species required for the model, use the **Add** (➕) and **Delete** ≡ₓ) 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.

Pressure constraint on edges are available for use with the Fracture Flow boundary condition (which is available in the Subsurface Flow Module). This boundary condition needs constraints on the edges surrounding the fracture-flow boundary. In other cases, pressure constraints on edges are not implemented.

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: $kg/(m^2 \cdot s)$).

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

Enter a value or expression for the source strength, N_0 (SI unit: kg/(m·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.

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 6-9) and N_0 is a specified value or expression for the flux discontinuity.

$$\mathbf{u} = -\frac{\kappa}{\mu} \nabla p \qquad (6\text{-}9)$$

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·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 two 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).

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.

This feature requires a specific license. For a detailed overview of the functionality available in each product visit http://www.comsol.com/products/specifications/.

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 (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.

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.

This feature requires a specific license. For a detailed overview of the functionality available in each product visit http://www.comsol.com/products/specifications/.

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.

This feature requires a specific license. For a detailed overview of the functionality available in each product visit http://www.comsol.com/products/specifications/.

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).

The Subsurface Flow Module license is required to use this boundary condition (see http://www.comsol.com/products/specifications/).

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.

The Subsurface Flow Module license is required to use this boundary condition (see http://www.comsol.com/products/specifications/).

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 $p = 0$.

The Subsurface Flow Module license is required to use this boundary condition (see http://www.comsol.com/products/specifications/).

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 Subsurface Flow Module license is required to use this boundary condition (see http://www.comsol.com/products/specifications/).

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:

$$\mathbf{n} \cdot \rho \frac{\kappa}{\mu}(\nabla p + \rho g \nabla D) = \rho R_b \left[\frac{(p_b - p)}{\rho g} + (D_b - D) \right] \tag{6-10}$$

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:

$$\mathbf{n} \cdot \rho K \nabla(H_p + D) = \rho R_b [(H_{pb} - H_p) + (D_b - D)] \tag{6-11}$$

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:

$$\mathbf{n} \cdot \rho K \nabla H = \rho R_b [H_b - H] \tag{6-12}$$

H_b is the hydraulic head (SI unit: m) at the edge of the layer.

K in Equation 6-11 and Equation 6-12 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_{pb} (SI unit: m), H_{pb} (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 well.

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 Flow

The **Fracture Flow** node adds fracture flow on boundaries using tangential derivatives to define the flow along interior boundaries representing fractures within a porous medium. It is implemented through . Additional subnodes are available from the context menu (right-click the parent node) or from the **Physics** toolbar, **Attributes** menu.

This feature requires a specific license. For a detailed overview of the functionality available in each product visit http://www.comsol.com/products/specifications/.

The Free and Porous Media Flow Interface

The **Free and Porous Media Flow (fp)** interface (![icon]), found under the **Porous Media and Subsurface Flow** branch (![icon]) when adding a physics interface, 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 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 **Fluid and Matrix Properties** 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** 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 **Compressible flow (Ma<0.3)** from the **Compressibility** list, to account for small

variations in the density, typically dependent on the temperature (nonisothermal flow). For compressible flow modeled with this physics interface, the Mach number must be below 0.3.

Neglect Inertial Term
Select the **Neglect inertial term (Stokes flow)** check box if the inertial forces are small compared to the viscous forces.

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].

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 Interface
- Theory for the Free and Porous Media Flow Interface

Domain, Boundary, Point, and Pair Nodes for the Free and Porous Media Flow Interface

The Free and Porous Media Flow 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-Electrolyte Interface Coupling
- Fluid Properties
- Initial Values
- Mass Source

- Porous Electrode Coupling
- Fluid and Matrix Properties
- Mass Source
- Volume Force
- Wall

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.

FLUID PROPERTIES

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.

Fluid and Matrix Properties

Use the **Fluid and Matrix Properties** node to define which domains contain porous material and to define the porous matrix properties, such as the porosity and permeability in these domains.

DOMAIN SELECTION

Choose domains from the **Selection** list, to solve for porous media flow governed by the Brinkman equations. In the domains not selected, the Free and Porous Media Flow interface solves for laminar flow governed by the Navier-Stokes (or Stokes) equations.

POROUS MATRIX PROPERTIES

The default **Porous material** uses the **Domain material** for the porous matrix. Select another material as needed.

The **Porosity** ε_p (a dimensionless number between 0 and 1) uses by default the value **From material** as defined by the **Porous material** selection. For **User defined** the default is 0.

> ⚠️ In this node you specify the porosity ε_p, whereas in other nodes the volume fraction of solid material $\theta_p = 1 - \varepsilon_p$ is required instead. See Porous Medium in the *Heat Transfer Module User's Guide* for an example.

Select a **Permeability model** to specify the capacity of the porous material to transmit flow — **Permeability** to directly enter the permeability of the porous matrix, **Kozeny-Carman** to define the permeability from the porosity and mean particle diameter, or **Non-Darcian** in cases when Darcy's linear relation between pressure drop and velocity is no longer valid due to turbulence or inertial effects. The **Non-Darcian Flow** option is 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 http://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**, **Symmetric**, or **Full** to define a tensor value and enter another value or expression in the field or matrix.

For **Kozeny-Carman**, enter the mean **Particle diameter** d_p (SI unit: m), the default value is 0.5 mm.

For **Non-Darcian**, choose a **Non-Darcian flow model** from the selection list. The available options, depend on the modules licensed, are **Forchheimer** or **Ergun**.

For **Forchheimer**, the default **Permeability** κ (SI unit: m^2) uses the value **From material**, as defined by the **Porous material** list. 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 .

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.

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 the Porous Matrix Properties node is active for the domain. Use it, for example, to incorporate the effects of gravity in a model.

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** ▤) 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.

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.

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**.

Q | - The Moving Mesh Interface in the *COMSOL Multiphysics Reference Manual*

Theory for the Laminar Flow and Creeping Flow Interfaces

The theory for the Single-Phase Flow, Laminar Flow and Viscoelastic Flow interfaces is described in this section:

- General Single-Phase Flow Theory
- Compressible Flow
- Weakly Compressible Flow
- The Mach Number Limit
- Incompressible Flow
- The Reynolds Number
- Theory for the Wall Boundary Condition
- Prescribing Inlet and Outlet Conditions
- Fully Developed Flow (Inlet)
- Fully Developed Flow (Outlet)
- No Viscous Stress
- Normal Stress Boundary Condition
- Mass Sources for Fluid Flow
- Numerical Stability — Stabilization Techniques for Fluid Flow
- Solvers for Laminar Flow
- Pseudo Time Stepping for Laminar Flow Models
- Discontinuous Galerkin Formulation
- 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

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \tag{6-13}$$

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot [-p\mathbf{I} + \tau] + \mathbf{F} \tag{6-14}$$

$$\rho C_p \left(\frac{\partial T}{\partial t} + (\mathbf{u} \cdot \nabla) T \right) = -(\nabla \cdot \mathbf{q}) + \tau{:}\mathbf{S} - \frac{T}{\rho} \frac{\partial \rho}{\partial T} \bigg|_p \left(\frac{\partial p}{\partial t} + (\mathbf{u} \cdot \nabla) p \right) + Q \tag{6-15}$$

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)
- τ 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

$$\mathbf{a}{:}\mathbf{b} = \sum_n \sum_m a_{nm} b_{nm} \tag{6-16}$$

This is sometimes referred to as the double dot product.

Equation 6-13 is the continuity equation and represents conservation of mass.
Equation 6-14 is a vector equation which represents conservation of momentum.
Equation 6-15 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 6-13 through Equation 6-15, constitutive relations are needed. For a Newtonian fluid, which has a linear relationship between stress and strain, Stokes (Ref. 1) deduced the following expression:

$$\tau = 2\mu\mathbf{S} - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I} \tag{6-17}$$

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. Examples of non-Newtonian fluids are honey, mud, blood, liquid metals, and most polymer solutions. The Heat Transfer Module treats all fluids as Newtonian according to Equation 6-17.Other commonly used constitutive relations are Fourier's law of heat conduction and the ideal gas law.

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 6-15 is decoupled from Equation 6-13 and Equation 6-14.

2D AXISYMMETRIC FORMULATIONS

A 2D axisymmetric formulation of Equation 6-13 and Equation 6-14 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 6-14. 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 6-13 and Equation 6-14 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:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \tag{6-18}$$

and the momentum equation:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \nabla \cdot \left(\mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) \mathbf{I} \right) + \mathbf{F} \tag{6-19}$$

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, Ma, defined by

$$\mathrm{Ma} = \frac{|\mathbf{u}|}{a}$$

where a is the speed of sound. A flow is formally incompressible when $\mathrm{Ma} = 0$. 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 6-19, is parabolic for unsteady flow and elliptic for steady flow, whereas the continuity equation, Equation 6-18, 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 6-19 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.

The practical Mach number limit is lower than one, however. 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 $Ma = 0.3$. 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 6-18 reduces to

$$\rho \nabla \cdot \mathbf{u} = 0 \qquad (6\text{-}20)$$

and Equation 6-19 becomes

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla)\mathbf{u} = \nabla \cdot [-p\mathbf{I} + \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T)] + \mathbf{F} \qquad (6\text{-}21)$$

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:

$$\text{Re} = \frac{\rho U L}{\mu}$$

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.

Observe 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 $\text{Re}^c = \rho|\mathbf{u}|h/(2\mu)$ 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`).

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:

$$\mathbf{u} \cdot \mathbf{n} = 0, \qquad (-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^{\mathrm{T}}))\mathbf{n} = \mathbf{0}$$

The no-penetration term takes precedence over the Neumann part of the condition and the above expression is therefore equivalent to

$$\mathbf{u} \cdot \mathbf{n} = 0, \qquad \mathbf{K} - (\mathbf{K} \cdot \mathbf{n})\mathbf{n} = \mathbf{0}$$
$$\mathbf{K} = \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^{\mathrm{T}})\mathbf{n}$$

expressing that there is no flow across the boundary and no viscous stress in the tangential direction.

For a moving wall with translational velocity $\mathbf{u}_{\mathrm{tr}}$, $\mathbf{u}$ in the above equations is replaced by the relative velocity $\mathbf{u}_{\mathrm{rel}} = \mathbf{u} - \mathbf{u}_{\mathrm{tr}}$.

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

$$\mathbf{u} \cdot \mathbf{n} = 0, \qquad \mathbf{u} \cdot \mathbf{t} = U_{\mathrm{w}}$$

  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 $\mathbf{u}_{\mathrm{w}}$ projected onto the boundary plane:

$$\mathbf{u} \;=\; \frac{\mathbf{u}_\mathrm{w} - (\mathbf{n} \cdot \mathbf{u}_\mathrm{w})\mathbf{n}}{\left\| \mathbf{u}_\mathrm{w} - (\mathbf{n} \cdot \mathbf{u}_\mathrm{w})\mathbf{n} \right\|} \left\| \mathbf{u}_\mathrm{w} \right\|$$

The normalization makes $\mathbf{u}$ have the same magnitude as $\mathbf{u}_\mathrm{w}$ even if $\mathbf{u}_\mathrm{w}$ is not exactly parallel to the wall.

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.

• Using 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*.

• Discontinuous Galerkin (DG) constraints use a numerical flux to prescribe the velocity at the wall. They impose the constraint in a 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 Discontinuous Galerkin Formulation.

The following combination of Constraint techniques can be selected in the Constraint Setting sections of Wall boundary conditions:

- Use default settings. The default settings 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.

  DG 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 DG constraints are used.

- Use Pointwise constraints.
- Use DG constraints.
- Use Weak constraints. Weak constraints are not available on Interior Walls.
- Use 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 DG 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:

$$-p + 2\mu\frac{\partial u_n}{\partial n} = F_n \qquad\qquad (6\text{-}22)$$

where $\partial u_n/\partial n$ is the normal derivative of the normal velocity component.

Equation 6-22 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 6-22 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 6-22, 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 permit 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.

Q Normal Stress Boundary Condition

Fully Developed Flow (Inlet)

The **Fully developed flow** boundary condition can be understood from the following figure:

p_inl | [dashed box] | Ω

L
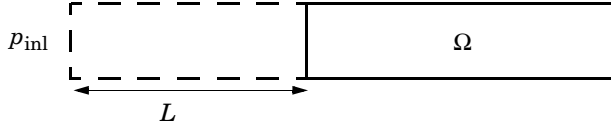
The flow to the domain Ω is assumed to enter through a straight channel of length L. The channel is a virtual extrusion of the inlet cross section and a pressure constant pressure P_inl is applied on the inlet of the virtual channel.

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:

$$(-\mu(\nabla_\mathbf{t}\mathbf{u} + (\nabla_\mathbf{t}\mathbf{u})^T) + p)\nabla_\mathbf{t}\hat{\mathbf{u}}L - P_\mathrm{inl}(\mathbf{n} \cdot \hat{\mathbf{u}})$$

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

$$(\langle \mathbf{u} \cdot \mathbf{n} \rangle + U_{av}) \hat{P}_{inl}$$

where $\langle \cdot \rangle$ 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 pre- and post-smoother if iterative solvers are employed.

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 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:
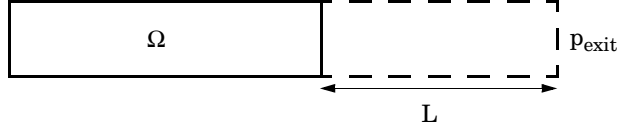
The flow to the domain Ω is assumed to enter through a straight channel of length L. The channel is a virtual extrusion of the inlet cross section and a pressure constant pressure P_{exit} is applied on the inlet of the virtual channel.

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:

$$(-\mu(\nabla_{\mathbf{t}}\mathbf{u} + (\nabla_{\mathbf{t}}\mathbf{u})^T) + p)\nabla_{\mathbf{t}}\hat{\mathbf{u}}L - P_{exit}(\mathbf{n} \cdot \hat{\mathbf{u}})$$

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 outlett 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 pre- and post-smoother if iterative solvers are employed.

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

$$p = 2\mu\frac{\partial u_n}{\partial n} + f_0 \tag{6-23}$$

If $\partial u_n/\partial n$ is small, Equation 6-23 states that $p \approx f_0$.

The Normal Stress condition is the mathematically correct version of the 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

$$\left(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right)\mathbf{n} = -p_0\mathbf{n} \tag{6-24}$$

$$(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T))\mathbf{n} = -p_0\mathbf{n} \tag{6-25}$$

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 6-24 or Equation 6-25 can be supplemented with a tangential velocity condition

$$\mathbf{u} \cdot \mathbf{t} = 0 \tag{6-26}$$

If so, the no-tangential-stress condition is overridden. An issue with Equation 6-24 or Equation 6-25 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

$$
\begin{gathered}
\left(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right)\mathbf{n} = -\hat{p}_0\mathbf{n} \\
(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T))\mathbf{n} = -\hat{p}_0\mathbf{n} \\
\hat{p}_0 \leq p_0
\end{gathered}
\qquad , \tag{6-27}
$$

the normal stress is adjusted to keep

$$\mathbf{u} \cdot \mathbf{n} \geq 0 \qquad (6\text{-}28)$$

Equation 6-27 effectively means that the prescribed pressure is p_0 if $\mathbf{u} \cdot \mathbf{n} \geq 0$, but smaller at locations where $\mathbf{u} \cdot \mathbf{n} < 0$. This means that Equation 6-27 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

$$\mathbf{n}^T\left(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right)\mathbf{n} = -\hat{p}_0$$

$$\mathbf{n}^T(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T))\mathbf{n} = -\hat{p}_0 \qquad (6\text{-}29)$$

$$\hat{p}_0 \geq p_0$$

together with the tangential condition in Equation 6-26, or, a general flow direction is prescribed.

$$\mathbf{r}_{\mathbf{u}}^T\left(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right)\mathbf{n} = -\hat{p}_0(\mathbf{r}_{\mathbf{u}} \cdot \mathbf{n})$$

$$\mathbf{r}_{\mathbf{u}}^T(-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T))\mathbf{n} = -\hat{p}_0(\mathbf{r}_{\mathbf{u}} \cdot \mathbf{n})$$

$$\hat{p}_0 \geq p_0 \qquad (6\text{-}30)$$

$$\mathbf{u} - (\mathbf{u} \cdot \mathbf{r}_{\mathbf{u}})\mathbf{r}_{\mathbf{u}} = \mathbf{0}, \ \mathbf{r}_{\mathbf{u}} = \frac{\mathbf{d}_{\mathbf{u}}}{\|\mathbf{d}_{\mathbf{u}}\|}$$

The ">" option is used with suppress backflow to have $\mathbf{u} \cdot \mathbf{n} \leq 0$ or $\mathbf{u} \cdot \mathbf{r}_{\mathbf{u}} \geq 0$.

See Inlet, Outlet, Open Boundary, and for the individual node settings. Note that some modules have additional theory sections describing options available with that module.

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: Batteries & Fuel Cells Module, CFD Module, Chemical Reaction Engineering Module, Corrosion Module, Electrochemistry Module, Electrodeposition Module, Microfluidics Module, Pipe 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

$$\lim_{\delta V \to 0} \int_{\delta V} \dot{Q} = \dot{q}_p \tag{6-31}$$

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 6-31, $\dot{Q}$ 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 6-31 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, $\dot{q}_1$ (SI unit: $kg/(m \cdot s)$), this can be expressed as

$$\lim_{\delta S \to 0} \int_{\delta S} \dot{Q} = \dot{q}_1 \tag{6-32}$$

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

$$\dot{q}_1 \text{test}(p)$$

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 Batteries & Fuel Cells 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 6-19 or Equation 6-21) 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. The time-scale tensor is the diagonal tensor presented in Ref. 10.

The time-scale tensors 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 doesn't 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. COMSOL Multiphysics can therefore replace Δt^2 in the time scale tensor with measures of type $(1/(\widetilde{\Delta t})^2)^{-1}$ 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 timescale** check box is selected. 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.

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.

🔍   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 Mutligrid (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, Geometric Multigrid (GMG) 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 which 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 6-21 reduces to:

$$\rho(\mathbf{u} \cdot \nabla)\mathbf{u} = \nabla \cdot [-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T)] + \mathbf{F} \qquad (6\text{-}33)$$

Solving Equation 6-33 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 6-33:

$$\rho \frac{\mathbf{u} - \text{nojac}(\mathbf{u})}{\Delta \tilde{t}} + \rho(\mathbf{u} \cdot \nabla)\mathbf{u} = \nabla \cdot [-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T)] + \mathbf{F}$$

where $\Delta \tilde{t}$ is a *pseudo time step*. Since $\mathbf{u} - \text{nojac}(\mathbf{u})$ 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:

$$\Delta \tilde{t} = \text{CFL}_{\text{loc}} \frac{h}{|\mathbf{u}|}$$

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 CFL_{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 CFL_{loc} as the solution comes closer to convergence.

The default manual expression is

$$
\begin{aligned}
& 1.3^{\min(\text{niterCMP},\, 9)} + \\
& \text{if}(\text{niterCMP} > 20,\, 9 \cdot 1.3^{\min(\text{niterCMP} - 20,\, 9)},\, 0) + \\
& \text{if}(\text{niterCMP} > 40,\, 90 \cdot 1.3^{\min(\text{niterCMP} - 40,\, 9)},\, 0)
\end{aligned}
\tag{6-34}
$$

The variable niterCMP is the nonlinear iteration number. It is equal to one for the first nonlinear iteration. CFL_{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 6-34 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.

Discontinuous Galerkin Formulation

Some boundary conditions are implemented using a discontinuous Galerkin formulation. 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 COMSOL Multiphysics is 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 in COMSOL Multiphysics 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 Brinkman Equations Interface

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:

$$\frac{\partial}{\partial t}(\varepsilon_p \rho) + \nabla \cdot (\rho \mathbf{u}) = Q_m \tag{6-35}$$

$$\frac{\rho}{\varepsilon_p}\left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\frac{\mathbf{u}}{\varepsilon_p}\right) =$$

$$-\nabla p + \nabla \cdot \left[\frac{1}{\varepsilon_p}\left\{\mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right\}\right] - \left(\kappa^{-1}\mu + \frac{Q_m}{\varepsilon_p^2}\right)\mathbf{u} + \mathbf{F} \tag{6-36}$$

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 6-36 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 6-36; see Permeability Models and Non-Darcian Flow for details.

In case of a flow with variable density, Equation 6-35 and Equation 6-36 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 6-35) reduces to

$$\rho \nabla \cdot \mathbf{u} = Q_m$$

References for the Brinkman Equations Interface

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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 Model
- Hydraulic Head, Pressure Head, and Elevation Head
- Average Linear Velocity
- Permeability Models and Non-Darcian Flow
- 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:

$$\mathbf{u} = -\frac{\kappa}{\mu}\nabla p \qquad (6\text{-}37)$$

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).

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. Visualize the hydraulic potential field by considering the difference in both pressure and elevation potential from the start to the end points of the flow line. According to Darcy's law, the net flux across a face of porous surface is

$$\mathbf{u} = -\frac{\kappa}{\mu}(\nabla p + \rho\mathbf{g}) \qquad (6\text{-}38)$$

In this equation $\mathbf{g}$ is the vector of gravitational acceleration. Furthermore, in the Subsurface Flow Module, $\mathbf{g}$ can be defined as $\mathbf{g} = -g\nabla D$ where g is the magnitude of gravitational acceleration (SI unit: m/s^2), D is the elevation (SI unit: m), and ∇D is a unit vector in the direction over which the gravity acts. Here the permeability κ

represents the resistance to flow over a representative volume consisting of many solid grains and pores.

The Darcy's Law interface combines Darcy's law with the continuity equation

$$\frac{\partial}{\partial t}(\rho\varepsilon_p) + \nabla \cdot (\rho\mathbf{u}) = Q_m \tag{6-39}$$

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.

Storage Model

Inserting Darcy's law (Equation 6-38) into the continuity equation produces the generalized governing equation

$$\frac{\partial}{\partial t}(\rho\varepsilon_p) + \nabla \cdot \rho\left[-\frac{\kappa}{\mu}(\nabla p)\right] = Q_m \tag{6-40}$$

Represent this equation fully in COMSOL Multiphysics because relationships between density or permeability can be freely specified, for example, and pressure, temperature, concentration, and so on.

Expand the time-derivative term in Equation 6-40

$$\frac{\partial}{\partial t}(\rho\varepsilon_p) = \varepsilon_p\frac{\partial\rho}{\partial t} + \rho\frac{\partial\varepsilon_p}{\partial t}$$

Define the porosity and the density as functions of the pressure, and apply the chain rule

$$\varepsilon_p \frac{\partial \rho}{\partial t} + \rho \frac{\partial \varepsilon_p}{\partial t} = \varepsilon_p \frac{\partial \rho}{\partial p} \frac{\partial p}{\partial t} + \rho \frac{\partial \varepsilon_p}{\partial p} \frac{\partial p}{\partial t}$$

Insert the definition of fluid compressibility $\chi_f = (1/\rho)(\partial \rho/\partial p)$ to the right-hand side and rearrange to arrive at

$$\frac{\partial(\rho \varepsilon_p)}{\partial t} = \rho \left(\varepsilon_p \chi_f + \frac{\partial \varepsilon_p}{\partial p} \right) \frac{\partial p}{\partial t} = \rho S \frac{\partial p}{\partial t}$$

Using this relation, the generalized governing equation (Equation 6-40) takes the following form:

$$\rho S \frac{\partial p}{\partial t} + \nabla \cdot \rho \left[-\frac{\kappa}{\mu} (\nabla p + \rho g \nabla D) \right] = Q_m \tag{6-41}$$

In this equation, S is the storage coefficient (SI unit: 1/Pa), which can be interpreted as the weighted compressibility of the porous material and the fluid. The storage S 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 6-41 using the Storage Model node, which explicitly includes an option to define S as the *linearized storage* (SI unit: 1/Pa) using the compressibility of fluids and porous matrix.

> Note that the Storage Model node is 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 http://www.comsol.com/products/specifications/.

Hydraulic Head, Pressure Head, and Elevation Head

Hydraulic head, H, pressure head, H_p, and elevation head, D, relate to pressure p as

$$H_p = \frac{p}{\rho g}; \quad H = H_p + D \tag{6-42}$$

where ρ is the fluid density, g denotes the acceleration of gravity, and D is the elevation. When defined as vertical elevation, the horizontal gradients in D equal zero and vertical gradients in D equal one. Choose to specify pressure, hydraulic head, or pressure head on the boundaries of a model, either directly or as part of the pervious

layer boundary condition. Also use pressure, hydraulic head, and pressure head during analysis and postprocessing.

📋	• Turning off gravity effects sets the elevation D to zero, and the hydraulic head equals the pressure head. • This feature is only available with the Subsurface Flow Module

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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, $\mathbf{u}$, 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.

Permeability Models and Non-Darcian Flow

Different models can define the capacity of the porous medium to transmit flow. Some use the permeability, κ, and the viscosity of the fluid, μ, and others use the hydraulic conductivity, K (SI unit: m/s).

HYDRAULIC CONDUCTIVITY

The hydraulic conductivity represents both fluid and solid properties. If the model is defined using the hydraulic conductivity as in:

$$\frac{\kappa}{\mu} = \frac{K}{\rho g}$$

Equation 6-38 changes to

$$\mathbf{u} = -\frac{\mathbf{K}}{\rho g}(\nabla p + \rho g \nabla D) \tag{6-43}$$

The hydraulic potential in the equation comes from the pore pressure, p, and gravity, $\rho g D$. COMSOL Multiphysics solves for the pressure, p. By default, g is the predefined acceleration of gravity (a physical constant), and D is the vertical coordinate. The choice of D has a significant impact on results and the physics involved. For example, if D is the vertical coordinate z and if the flow is entirely horizontal within the xy-plane, then the gradient in D vanishes and the driving force is caused by pressure gradients alone.

KOZENY-CARMAN

The Kozeny-Carman equation describes the flow through granular soils and packed beds by estimating the permeability of the porous medium from the porosity ε_p and average particle diameter d_p (see, for example, Ref. 5)

$$\kappa = \frac{d_p^2}{180} \frac{\varepsilon_p^3}{(1-\varepsilon_p)^2}$$

If the model is defined using the Kozeny-Carman equation, the expression for Darcy's velocity in Equation 6-38 changes to

$$\mathbf{u} = -\frac{d_p^2}{180\mu} \frac{\varepsilon_p^3}{(1-\varepsilon_p)^2} (\nabla p) \tag{6-44}$$

> The hydraulic conductivity combines properties of both the fluid and porous matrix, while the permeability is a property of the porous matrix only.

In case of relatively fast flow ($\mathrm{Re} > 10$) or relatively high Knudsen numbers ($\mathrm{Kn} > 0.1$) Darcy's linear relation between velocity and pressure drop is no longer valid. Therefore, different permeability models have been introduced to capture these effects.

The flow regime through a packed bed may be identified from the Reynolds number of the bed. According to textbooks, for Reynolds numbers $\mathrm{Re} < 10$ the flow can be described by Kozeny-Carman equation (Darcian flow). For $10 < \mathrm{Re} < 1000$, which is sometimes called the *transitional regime*, the flow is better described by the non-Darcian Ergun equation, and for $\mathrm{Re} > 1000$ Ergun's equation can be approximated by the Burke-Plummer equation for turbulent flows.

ERGUN

The Ergun equation is an extension of Kozeny-Carman equation to higher Reynolds numbers ($\mathrm{Re} > 10$), where Darcy's linear relation between pressure drop and velocity is no longer valid. In Ergun equation the linear relation between pressure drop and velocity is augmented by a quadratic term. The pressure drop (Ref. 6) in Ergun's equation is given by:

$$-\nabla p = \frac{150(1-\varepsilon_p)^2}{d_p^2} \frac{1}{\varepsilon_p^3}\mu\mathbf{u} + \frac{1.75}{d_p}\frac{(1-\varepsilon_p)}{\varepsilon_p^3}\rho\mathbf{u}|\mathbf{u}| \qquad (6\text{-}45)$$

Here, d_p is the effective (average) particle diameter in the porous medium and ε_p is the porosity. With definitions of permeability κ and parameter β (SI unit 1/m) as

$$\kappa = \frac{d_p^2}{150}\frac{\varepsilon_p^3}{(1-\varepsilon_p)^2} \qquad (6\text{-}46)$$

and

$$\beta = \frac{1.75}{d_p}\frac{(1-\varepsilon_p)}{\varepsilon_p^3} \qquad (6\text{-}47)$$

we get

$$\nabla p = -\frac{\mu}{\kappa}\mathbf{u} - \beta\rho|\mathbf{u}|\mathbf{u}$$

Ergun's velocity can then be calculated as

$$\mathbf{u} = -\frac{\kappa}{\mu}\frac{2}{1 + \sqrt{1 + 4\left(\frac{\kappa}{\mu}\right)^2 \beta\rho|\nabla p|}}\nabla p \qquad (6\text{-}48)$$

Using the Reynolds number Re and the friction factor f_p for packed beds

$$\mathrm{Re} = \frac{d_p\rho|\mathbf{u}|}{(1-\varepsilon_p)\mu}$$

$$f_p = |\nabla p|\frac{d_p}{\rho\mathbf{u}^2}\frac{\varepsilon_p^3}{(1-\varepsilon_p)} = \frac{150}{\mathrm{Re}} + 1.75\,,$$

Ergun's velocity can alternatively be written as

$$\mathbf{u} = -\frac{\kappa}{\mu}\frac{1}{1 + \frac{1.75}{150}\mathrm{Re}}\nabla p = -\frac{\kappa}{\mu}\left(1 - \frac{1.75}{f_p}\right)\nabla p$$

From this expression, we observe that for low Reynolds numbers $\mathrm{Re} < 1$ (or equivalently, high friction factors) the flow can be described by the linear Darcy's Law.

FORCHHEIMER

For increasing filter velocities ($\text{Re} > 10$), inertial effects and turbulent friction forces become significant. In the Forchheimer drag this is considered by adding an additional term to Darcy's law:

$$-\nabla p \;=\; \frac{\mu}{\kappa}\mathbf{u} + \frac{c_F}{\sqrt{\kappa}}\rho\mathbf{u}|\mathbf{u}| \tag{6-49}$$

Here, the Forchheimer parameter c_F is dimensionless. The permeability κ is specified by the user and is not computed from porosity nor particle diameter as for Ergun's equation. If the parameter β is defined as

$$\beta \;=\; \frac{c_F}{\sqrt{\kappa}}$$

Equation 6-49 becomes equivalent to Ergun's equation (Equation 6-45)

$$-\nabla p \;=\; \frac{\mu}{\kappa}\mathbf{u} + \beta\rho\mathbf{u}|\mathbf{u}|$$

BURKE-PLUMMER

The Burke-Plummer equation is applicable in flow regimes with Reynolds number $\text{Re} > 1000$. Here, the pressure drop is proportional to the square of the velocity:

$$\frac{\Delta p}{L} \;=\; 1.75\frac{(1-\varepsilon_p)}{d_p}\frac{1}{\varepsilon_p^3}\rho v^2 \tag{6-50}$$

here, L is the length of the packed bed, Δp is the pressure drop d_p is the effective (average) particle diameter in the porous medium, ε_p is the porosity, and v is the velocity magnitude.

Using the same definition for the parameter β (SI unit $1/m$) as in Ergun's equation

$$\beta \;=\; \frac{1.75}{d_p}\frac{(1-\varepsilon_p)}{\varepsilon_p^3}$$

the pressure drop is related to the velocity as

$$\frac{\Delta p}{L} \;=\; \beta\rho v^2 \tag{6-51}$$

which means that the velocity magnitude can be written in terms of the pressure gradient as

$$v = \sqrt{\frac{|\nabla p|}{\beta \rho}}$$

As flow travels from areas of higher pressure to areas of lower pressure, Equation 6-45 can be more generally written as

$$-\nabla p = \beta \rho |\mathbf{u}| \mathbf{u}$$

replacing

$$|\mathbf{u}| = v = \sqrt{|\nabla p| / \beta \rho}$$

we get an expression for the velocity field in terms of the pressure gradient

$$\mathbf{u} = -\frac{1}{\sqrt{\beta \rho |\nabla p|}} \nabla p \qquad (6\text{-}52)$$

Note that the viscosity is not used to define the velocity as in Darcy's law, but only the fluid density, the porosity and particle diameter. Note also that the analytical friction factor for Burke-Plummer equation is $f_p = 1.75$. A small parameter is added inside the square-root to avoid division by zero when the pressure gradient approaches zero.

KLINKENBERG

The Klinkenberg effect becomes important for gas flows in porous media where the mean free path of the gas molecules is comparable to the pore dimensions. In this case, molecular collisions with the pore walls occur more often than collisions between molecules. To take this effect into account, Klinkenberg (Ref. 7) derived the following expression for the permeability:

$$\kappa = \kappa_\infty \left(1 + \frac{b_K}{p_A} \right) \qquad (6\text{-}53)$$

here, κ_∞ is the permeability of the gas at high pressure and density (Knudsen number $0.001 < \mathrm{Kn} < 0.1$), b_K is the Klinkenberg parameter (also called *Klinkenberg slip factor*, or *gas slippage factor*), whose default value is set to 1 kPa according to Ref. 8, and p_A is the absolute pressure as defined in the Darcy's Law interface ($p_A = p + p_{\mathrm{ref}}$).

References for the Darcy's Law Interface

1. J. Bear, *Hydraulics of Groundwater*, McGraw-Hill, 1979.

2. S.E. Ingebritsen and W.E. Sanford, *Groundwater in Geologic Processes*, Cambridge University Press, 1998.

3. N.H. Sleep and K. Fujita, *Principles of Geophysics*, Blackwell Science, 1997.

4. D.L. Turcotte and G. Schubert, *Geodynamics*, Cambridge University Press, 2002.

5. J. Bear, *Dynamics of Fluids in Porous Media*, Elsevier Scientific Publishing, 1972.

6. Ö. Akgiray and A.M. Saatçı, "A New Look at Filter Backwash Hydraulics," *Water Science and Technology: Water Supply*, vol. 1, no. 2, pp. 65–72, 2001.

7. L. Klinkenberg, "The permeability of porous media to liquids and gases," *Drilling and Production Practice*, Am. Petroleum Inst., pp. 200–213, 1941.

8. Yu-Shu Wu et al., "Gas Flow in Porous Media with Klinkenberg Effects," *Transport in Porous Media*, vol. 32, pp. 117–137, 1998.

Theory for the Free and Porous Media Flow Interface

The Free and Porous Media Flow 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 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 Coupling of Fluid Flow to Electrochemical Reactions

Also see Coupling of Heat Transfer 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

$$\mathbf{u} \cdot \mathbf{n} = \frac{1}{\rho} \sum_i \mathbf{n}_i \cdot \mathbf{n} \tag{6-54}$$

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

$$\mathbf{u} = -\left(\frac{1}{\rho} \sum_i M_i N_i\right) \mathbf{n} \tag{6-55}$$

where M_i (SI unit: kg/mol) is the species mass and N_i (SI unit: mol/(m²·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:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = \sum_i R_{i,\,\text{mass}} \tag{6-56}$$

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 Corrosion Module also provides extra functionality for simulating heat transfer in porous media. The documentation of all features in The Heat Transfer in Porous Media Interface is found in the *Heat Transfer Module User's Guide*, which is supplied with the Corrosion Module irrespective of whether a separate Heat Transfer Module license is purchased.

In this chapter:

• Coupling of Heat Transfer to Electrochemical Reactions

Coupling of Heat Transfer to Electrochemical Reactions

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

In addition, reversible heat sources and sinks can appear due to the entropy changes in the electrode reactions. How these heat sources are defined are described at the end of this chapter.

Most Electrochemistry interfaces define and announce heat source variables that for instance 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 Electrochemical Heatingmultiphysics node that becomes available in the model builder tree under the **Multiphysics** node if there is both a Heat Transfer interface and an Electrochemistry interface available in the same component. It 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. It also sets the temperature in the electrochemistry interface to equal the temperature dependent variable in the heat transfer 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.

Q
- Electrochemistry Interfaces
- Multiphysics Coupling Nodes

Joule Heating Due to Charge Transport

The charge transport in the solid conductor material and electrolyte create joule heating source terms according to

$$Q_{JH} = -(\mathbf{i}_s \cdot \nabla \phi_s + \mathbf{i}_l \cdot \nabla \phi_l) \tag{7-1}$$

Heating Due to Electrochemical Reactions

For an electrochemical reaction process one can write the total heat balance as:

• Heat generated = Total reaction enthalpy – Electrical energy leaving the system

Using Faraday's law for an electrode reaction, m, at the interface between the electron and ion conducting phase this corresponds to

$$Q_m = \left(\frac{\Delta H_m}{n_m F} - \left(\frac{\Delta G_m}{n_m F} - \eta_{m, tot}\right)\right) i_m \tag{7-2}$$

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. The equilibrium potential is related to ΔG_m in the following way:

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

In Equation 7-2 we have used the total overpotential, $\eta_{m,tot,}$ (including potential effects from film resistances and similar), defined as

$$\eta_{m, tot} = \phi_s - \phi_l - E_{eq, m}$$

By the relation

$$\frac{\partial E_{eq, m}}{\partial T} = \frac{\Delta S_m}{n_m F}$$

the local heat source due to the electrochemical conversion process becomes

$$Q_m = \left(\eta_{m,\text{tot}} + T\frac{\partial E_{\text{eq},m}}{\partial T}\right)i_m$$

where the overpotential expression represents the irreversible activation losses, and the last term is the reversible heat change due to the net change of entropy in the conversion process.

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

$$Q_{\text{TOT},p} = \sum_m a_{v,m}Q_m + Q_{JH}$$

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,

$$n_m \; = \; \alpha_{a,\,m} + \alpha_{c,\,m}$$

is assumed.

The above concentration overpotential addition to the total overpotential is also used for the Electroanalytical Butler-Volmer kinetics in the Electroanalysis interface.

8

Mathematics, Moving Interface Branch

This chapter describes the Level Set interface, found under the
Mathematics>Moving Interface branch (▮).

In this chapter:

- The Level Set Interface
- Theory for the Level Set Interface

The Level Set Interface

The **Level Set (ls)** interface (〰〰), found under the **Mathematics>Moving Interface** branch (▮) when adding an interface, is used to track moving interfaces in fluid-flow models by solving a transport equation for the level set function. Simulations using the **Level Set** interface are always time dependent since the position of an interface almost always depends on its history.

The main node is the Level Set Model feature, which adds the level set equation and provides an interface for defining the level set properties and the velocity field.

When this physics interface is added, the following default nodes are also added in the **Model Builder** — **Level Set Model**, **No Flow** (the default boundary condition) and **Initial Values**. Then, from the **Physics** toolbar, add other nodes that implement, for example, boundary conditions. You can also right-click **Level Set** 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 ls.

STABILIZATION

To display this sections, click the **Show More Options** button (👁) and select **Stabilization** in the **Show More Options** dialog box.

There are two stabilization methods available — **Streamline diffusion** and **Crosswind diffusion**. Both are active by default and should remain selected for optimal performance.

ADVANCED SETTINGS

To display this sections, click the **Show More Options** button (👁) and select **Advanced Physics Options** in the **Show More Options** dialog box.

Specify the **Convective term** as **Nonconservative form** (default) or **Conservative form**.

DISCRETIZATION

By default, the Level Set interface uses **Linear** elements.

DEPENDENT VARIABLES

The dependent variable (field variable) is the **Level set variable** phi. The name can be changed but the names of fields and dependent variables must be unique within a model.

Q
- Conservative and Nonconservative Form
- Domain, Boundary, and Pair Nodes for the Level Set Interface
- Theory for the Level Set Interface

Domain, Boundary, and Pair Nodes for the Level Set Interface

The Level Set Interface has the following domain, boundary and pair nodes described.

- Continuity
- Initial Interface
- Initial Values
- Inlet
- Level Set Model
- No Flow
- Outlet[1]

- Periodic Condition (see Periodic Boundary Conditions in the *COMSOL Multiphysics Reference Manual*)
- Symmetry[1]
- Thin Barrier

[1] Described for the Laminar Flow interface.

Boundary conditions for axial symmetry boundaries are not required. For the symmetry axis at $r = 0$, the software automatically provides a suitable boundary condition 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.

Level Set Model

The **Level Set Model** node adds the following transport equation governing a level set function ϕ

$$\frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = \gamma \nabla \cdot \left(\varepsilon \nabla \phi - \phi(1 - \phi) \frac{\nabla \phi}{|\nabla \phi|} \right)$$

and provides the options to define the associated level set parameters and the velocity field.

LEVEL SET PARAMETERS

Enter a value or expression for the **Reinitialization parameter** γ (SI unit: m/s). The default is 1 m/s.

Enter a value or expression for the **Parameter controlling interface thickness** e_{ls} (SI unit: m). The default expression is `ls.hmax/2`, which means that the value is half of the maximum mesh element size in the region through which the interface passes.

CONVECTION

Enter values or expressions for the components (u, v, and w in 3D, for example) of the **Velocity field u** (SI unit: m/s). The applied velocity field transports the level set function through convection.

Initial Values

Use the **Initial Values** node to define the initial values of the level set variable.

INITIAL VALUES

The initial positions of the two fluids, and consequently the separating interface, can be specified in two ways. The level set function can be specified explicitly, using any type of variable or expression. Alternatively the fluid occupying the current domain selection can be specified. Using the former method, a Time Dependent study step can

directly be solved. Using the latter method, a Phase Initialization study step is needed in order to initialize the level set function across the fluid-fluid interface.

Specify the **Level set variable** as one of the following:

- To specify the fluid occupying the domain, select **Specify phase** (default). Then select the check box **Fluid 1 ($\phi = 0$)** or **Fluid 2 ($\phi = 1$)**.

- For **User defined** enter a value or expression for the level set variable ϕ.

> ⚠ If the **Phase Initialization** (⬚) study step is being used, for the initialization to work it is crucial that there are two Initial Values nodes and one Initial Interface node. The Initial Values nodes should specify the **Level set variable** as **Specify phase: Fluid 1** and **Specify phase: Fluid 2** respectively. The **Initial Interface** node should include all interior boundaries that define the initial position of the fluid-fluid interface. If the selection of the **Initial interface** node is empty, the initialization fails.
>
> See Initializing the Level Set Function.

Inlet

SETTINGS

Specify **Level Set Condition** according to one of the following options:

- **Fluid 1 ($\phi = 0$)**
- **Fluid 2 ($\phi = 1$)**
- **Specify level set function explicitly**

When the **Specify level set function explicitly** is selected, the level set function ϕ must be specified in the entire domain. The value must be in the range from 0 to 1, where the default is 0.

Initial Interface

The **Initial Interface** node defines the boundary as the initial position of the interface $\phi = 0$.

If the **Transient with Initialization** ( ) study is being used, for the initialization to work it is crucial that there are two Initial Values nodes and one Initial Interface node. One of the Initial Values nodes should use **Specify phase: Fluid 1** and the other **Specify phase: Fluid 2**. The Initial Interface node should have all interior boundaries where the interface is initially present as selection. If the selection of the **Initial interface** node is empty, the initialization fails.

See Initializing the Level Set Function.

A version of the **Initial Interface** suitable for pairs where the boundaries match is also available. It combines the initial interface feature with the Continuity feature, which prescribes that the level set variable is continuous across the pair. To add the pair version of the initial interface feature, right click the physics interface and select **Pairs>Initial Interface**.

No Flow

The **No Flow** node adds a boundary condition that represents boundaries where there is no flow across the boundary. This is the default boundary condition.

Thin Barrier

The **Thin Barrier** feature is available on interior boundaries and introduces a discontinuity in the level set variable across the boundary. A No Flow condition is prescribed on each side. This node can be used to avoid meshing thin structures.

Continuity

The **Continuity** condition is suitable for pairs where the boundaries match; it prescribes that the level set variable is continuous across the pair.

A No Flow subnode is added by default and it applies to the parts of the pair boundaries where a source boundary lacks a corresponding destination boundary and vice versa. The **No Flow** feature can be overridden by any other boundary condition that

applies to exterior boundaries. By right-clicking the **Continuity** node, additional Fallback feature subnodes can be added.

LOCATION IN USER INTERFACE

Right click the physics interface and select **Pairs>Continuity**

Ribbon
Physics tab with the physics interface selected:

Pairs>Continuity

Theory for the Level Set Interface

Fluid flow with moving interfaces or boundaries occur in a number of different applications, such as *fluid-structure interaction*, multiphase flows, and flexible membranes moving in a liquid. One way to track moving interfaces is to use a level set method. A certain contour line of the globally defined function, the level set function, then represents the interface between the phases. For the fluid-fluid interface can be advected with an arbitrary velocity field.

In this section:

- The Level Set Method
- Conservative and Nonconservative Form
- Initializing the Level Set Function
- Variables For Geometric Properties of the Interface
- Reference for the Level Set Interface

The Level Set Method

The *level set method* is a technique to represent moving interfaces or boundaries using a fixed mesh. It is useful for problems where the computational domain can be divided into two domains separated by an interface. Each of the two domains can consist of several parts. Figure 8-1 shows an example where one of the domains consists of two separated parts. The interface is represented by a certain level set or isocontour of a globally defined function, the level set function ϕ. In COMSOL Multiphysics, ϕ is a smooth step function that equals zero (0) in one domain and one (1) in the other. Across the interface, there is a smooth transition from zero to one. The interface is

defined by the 0.5 isocontour, or level set, of ϕ. Figure 8-2 shows the level set representation of the interface in Figure 8-1.
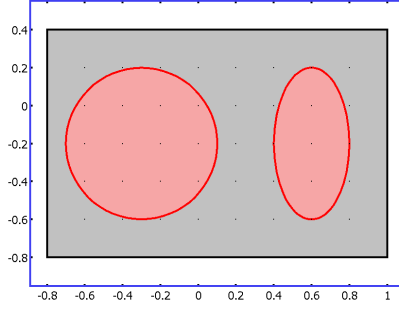
Figure 8-1: An example of two domains divided by an interface. In this case, one of the domains consists of two parts. Figure 8-2 *shows the corresponding level set representation.*
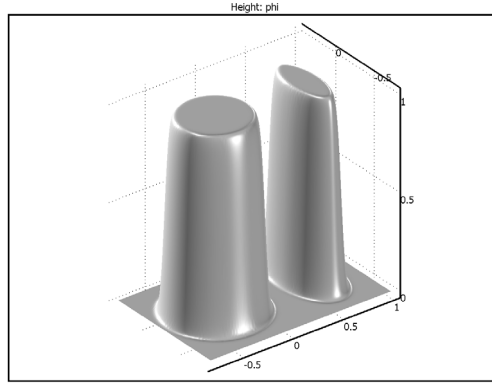
Figure 8-2: A surface plot of the level set function corresponding to Figure 8-1.

The physics interface solves Equation 8-1 in order to move the interface with the velocity field **u**:

$$\frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = \gamma \nabla \cdot \left(\varepsilon \nabla \phi - \phi(1-\phi)\frac{\nabla \phi}{|\nabla \phi|} \right) \tag{8-1}$$

The terms on the left-hand side give the correct motion of the interface, while those on the right-hand side are necessary for numerical stability. The parameter, ε, determines the thickness of the region where ϕ varies smoothly from zero to one and is typically of the same order as the size of the elements of the mesh. By default, ε is

constant within each domain and equals the largest value of the mesh size, h, within the domain. The parameter γ determines the amount of reinitialization or stabilization of the level set function. It needs to be tuned for each specific problem. If γ is too small, the thickness of the interface might not remain constant and oscillations in ϕ can appear because of numerical instabilities. On the other hand, if γ is too large the interface moves incorrectly. A suitable value for γ is the maximum magnitude of the velocity field $\mathbf{u}$.

Conservative and Nonconservative Form

If the velocity is divergence free, that is, if

$$\nabla \cdot \mathbf{u} = 0 \qquad (8\text{-}2)$$

the volume (area for 2D problems) bounded by the interface should be conserved if there is no inflow or outflow through the boundaries. To obtain exact numerical conservation in cases where Equation 8-2 is not fully satisfied, switch to the conservative form

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (\mathbf{u}\phi) = \gamma \nabla \cdot \left(\varepsilon \nabla \phi - \phi(1-\phi)\frac{\nabla \phi}{|\nabla \phi|} \right) \qquad (8\text{-}3)$$

in Settings window for .

Using the conservative level set form, exact numerical conservation of the integral of ϕ is obtained. However, the nonconservative form is better suited for numerical calculations and usually converges more easily. The nonconservative form, which is the default form, only conserves the integral of the level set function approximately, but this is sufficient for most applications.

Initializing the Level Set Function

If the study type Transient with Phase Initialization is used in the model, the level set variable is first initialized so that it varies smoothly between zero and one over the interface. For that study, two study steps are created, Phase Initialization and Time Dependent. The Phase Initialization step solves for the distance to the initial interface, D_{wi}. The Time Dependent step then uses the initial condition for the level set function according to the following expression:

$$\phi_0 = \frac{1}{1 + e^{-D_{\text{wi}}/\varepsilon}}$$

in domains initially outside the interface and

$$\phi_0 = \frac{1}{1 + e^{D_{wi}/\varepsilon}}$$

in domains initially inside the interface. Here, inside refers to domains where $\phi < 0.5$ and outside refers to domains where $\phi > 0.5$.

| ! | For the initialization to work it is crucial that there are two **Initial Values** nodes and one **Initial Interface** node. One of the Initial Values nodes should use **Specify phase: Fluid 1 ($\phi = 0$)** and the other **Specify phase: Fluid 2 ($\phi = 1$)**. The Initial Interface node should have all interior boundaries where the interface is initially present as selection. If the selection of the Initial interface node is empty, the initialization fails. |

| Q | • Studies and Solvers and Time Dependent with Initialization in the *COMSOL Multiphysics Reference Manual* |

Variables For Geometric Properties of the Interface

Geometric properties of the interface are often needed. The unit normal to the interface is given by

$$\mathbf{n} = \left.\frac{\nabla\phi}{|\nabla\phi|}\right|_{\phi = 0.5} \tag{8-4}$$

This variable is available in the physics interface as the interface normal `ls.intnorm`.

Reference for the Level Set Interface

1. E. Olsson and G. Kreiss, "A Conservative Level Set Method for Two Phase Flow," *J. Comput. Phys.*, vol. 210, pp. 225–246, 2005.

9

Multiphysics Coupling Nodes

The Corrosion 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.

🔍   The Multiphysics Branch in the *COMSOL Multiphysics Reference Manual*.

In this chapter, the following multiphysics couplings nodes are described:

- Deforming Electrode Surface
- Nondeforming Boundary
- Electrochemical Heating
- Potential Coupling
- Space Charge Density Coupling

Deforming Electrode Surface

Use the **Deforming Electrode Surface** multiphysics coupling to model deformation of the geometry due to an electrochemical deposition-dissolution process.

The node uses the deposition-dissolution velocity of an Electrode Surface boundary in a current distribution interface to apply a deformation velocity on to a boundary of a Free Deformation domain of a Deformed Geometry Interface.

Special conditions for the tangential velocity at points (2D) and edges (3D) shared with nondeforming surfaces apply, as described in the theory section.

The node, available as a multiphysics coupling node, can only be added to a component when there is both a Current Distribution and a Deformed Geometry interface present.

MOVING BOUNDARY SMOOTHING

Certain electrode deformation problems are inherently unstable. The Moving Boundary Smoothing will stabilize the moving boundary by applying a fictitious surface tension. Use the **Moving boundary smoothing tuning parameter,** δ_{mbs}, to control smoothing. A higher value means more smoothing.

RECOMMENDED SETTINGS IN THE COUPLED DEFORMED GEOMETRY INTERFACE

Predefined multiphysics interfaces are available from the model wizard that will automatically add and set up the coupling between a current distribution interface and the deformed geometry node. However, you can also add a Deformed Geometry interface manually to an already existing model.

The following settings are recommended in the Deformed Geometry interface if you are manually setting up the coupling between a Deformed Geometry interface and an Electrochemistry interface using the Deforming Electrode Surface and Nondeforming Boundary multiphysics coupling nodes:

• At the Deformed Geometry interface node, change the Geometry shape order to 1 and Mesh smoothing type to Hyperelastic

• Clear all the check boxes at the default Prescribed Mesh Displacement boundary feature node

- Add Free Deformation domain node and make sure it is selected on the deforming domains of the geometry

---

| 🔍 | Tangential Velocities at the Intersection Between a Depositing and a Noncorroding Boundary |

Nondeforming Boundary

Use the **Nondeforming Boundary** multiphysics coupling to define boundaries that do not undergo deformation in the normal direction.

A **Nondeforming Boundary** can be applied to external boundaries of an electrolyte and is typically used to specify an insulator, a nondissolving/depositing electrode surface or a symmetry boundary in a problem.

The node, available as a multiphysics coupling node, can only be added to a component when there is both a Current Distribution and a Deformed Geometry interface present.

Zero normal displacement is implemented using pointwise constraints, which may be more numerically stable, but should typically only be used for planar boundaries since the boundary is effectively fixed in the tangential direction if the curvature of the boundary is nonzero.

As a rule of thumb: use **Zero normal displacement** for planar boundaries and **Zero normal velocity** for curved boundaries.

For 3D components, and when **Zero normal displacement** is selected, the deformation may be further stabilized by enabling the **Allow deformation along specified line only**. The specified line must be parallel to the boundary in the nondeformed geometry.

See also the Deforming Electrode Surface node.

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*.

🔍 | Coupling of Heat Transfer to Electrochemical Reactions

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.

Boundary Electrolyte Potential Coupling

The Boundary Elements Potential Coupling node couples the electrolyte phase potential, computed in a finite-element-based (FEM) physics interface to the electrolyte phase potential of a boundary-element-based (BEM) physics interface.

COUPLED INTERFACES

Specify the FEM interface in the **Source** list and the BEM interface in the **Destination** list.

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Glossary

This Glossary of Terms contains application-specific terms used in the Corrosion 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 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.

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 Transport of Diluted Species interface. The Nernst-Planck equation is often combined with an electroneutrality condition, which can be modeled in COMSOL Multiphysics using the Tertiary Current Distribution, Nernst-Planck interface.

Nernst-Planck-Poisson equation In certain situations, for instance when striving to resolve the electrochemical double layer at an electrode, and electrokinetic flow 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.

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