

# Electrochemistry Module

User's Guide

# Electrochemistry Module User's Guide

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# Introduction

This guide describes the Electrochemistry Module, an optional add-on package for COMSOL Multiphysics®.

This chapter introduces you to the capabilities of this module including an introduction to the modeling stages and some realistic and illustrative models. 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 Electrochemistry Module](#)
- [Overview of the User's Guide](#)

# About the Electrochemistry Module

These topics are included in this section:

- [What Can the Electrochemistry Module Do?](#)
- [The Electrochemistry Module Physics Interface Guide](#)
- [Common Physics Interface and Feature Settings and Nodes](#)
- [Electrochemistry Module Study Availability](#)
- [Where Do I Access the Documentation and Application Libraries?](#)



[The Physics Interfaces and Building a COMSOL Multiphysics Model in the \*COMSOL Multiphysics Reference Manual\*](#)

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## *What Can the Electrochemistry Module Do?*

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The Electrochemistry Module extends the COMSOL Multiphysics environment with customized physics interfaces for modeling of electrochemical cells, with tools for building detailed models of the configuration of electrodes and electrolyte. The physics interfaces include descriptions of the electrochemical reactions and the transport properties that influence the behavior of various types of electrochemical cells. With this module, you have the perfect tools to investigate the influence of using different materials, geometric configurations, and operating conditions on the behavior of a cell.

The targeted applications for this module are the following:

- Electroanalysis
- Rotating disc electrodes
- Voltammetry
- Chronoamperometry
- Electrochemical impedance spectroscopy
- Electrochemical sensors
- Electrolysis
- Electrodialysis
- Biosensors
- Electrochemical nanotechnology

The physics interfaces include chemical species transport, charge balances, heat transfer, and fluid flow. You can use the module to model electrochemical and electroanalytical procedures in electrochemical cells at different operating conditions for different electrode configurations, structures and dimensions; and different electrode and electrolyte materials and chemistry.

The module adds the electrochemistry interfaces, which contains the Electroanalysis interface and the Primary Current Distribution, Secondary Current Distribution, and Tertiary Current Distribution, Nernst-Planck interfaces. The current distribution interfaces are available for solid nonporous electrodes and for porous electrodes. General tertiary current distribution models can also be set up using the Chemical Species Transport interfaces.

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

The physics interfaces for chemical species transport of neutral species are extended by adding functionality that directly couples to electrochemical reactions defined in the physics interfaces for electrochemical cells.

**Heat Transfer Interfaces** includes heat sources that describe ohmic losses in the electrodes and electrolyte and heat sources due to electrochemical reactions in electrochemical cells.

The fluid flow capabilities are extended for laminar flow, where the chemical species transport and the energy balances influence the properties of the flow.

### *The Electrochemistry Module Physics Interface Guide*

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The Electrochemistry Module extends the functionality of the physics interfaces for the base package of COMSOL Multiphysics. The details of the physics interfaces and study types for the Electrochemistry 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](#)
- [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 PRESET STUDY TYPE
 <b>Chemical Species Transport</b>				
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
Electrophoretic Transport		el	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization
Nernst-Planck-Poisson Equations		tds+es	all dimensions	stationary; time dependent; stationary source sweep; small-signal analysis, frequency domain



PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE PRESET STUDY TYPE
 <b>Electrochemistry</b>				
Primary Current Distribution		siec	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent
Secondary Current Distribution				
Tertiary Current Distribution, Nernst-Planck (Electroneutrality, Water-Based with Electroneutrality, Supporting Electrolyte)		tcdee	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	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, Shell		cdsh	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent
Electroanalysis		elan	all dimensions	stationary; time dependent; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent; cyclic voltammetry

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE PRESET STUDY TYPE
Electrode, Shell		els	3D, 2D, 2D axisymmetric	stationary; time dependent
 <b>Fluid Flow</b>				
 <b>Porous Media and Subsurface Flow</b>				
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
 <b>Heat Transfer</b>				
Heat Transfer in Porous Media		ht	all dimensions	stationary; time dependent

### *Common Physics Interface and Feature Settings and Nodes*

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

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



In the *COMSOL Multiphysics Reference Manual* see [Table 2-3](#) for links to common sections and [Table 2-4](#) 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.



TABLE I-1: MODULE DEPENDENT PHYSICS INTERFACES AND STUDY AVAILABILITY

PHYSICS INTERFACE	NAME	PRESET STUDIES*			
		STATIONARY	TIME DEPENDENT	AC IMPEDANCE STATIONARY	AC IMPEDANCE TIME DEPENDENT
Surface Reactions	sr	√	√		
Transport of Diluted Species	tds	√	√		
Transport of Diluted Species in Porous Media	tds	√	√		
Primary Current Distribution	siec	√			
Secondary Current Distribution	siec	√	√	√	√
Tertiary Current Distribution, Nernst-Planck	tcdee	√	√	√	√
Electroanalysis	elan	√	√	√	√
Laminar Flow	spf	√	√		
Brinkman Equations	br	√	√		
Darcy's Law	dl	√	√		
Free and Porous Media Flow	fp	√	√		
Heat Transfer in Porous Media	ht	√	√		
* Custom studies are also available					

*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 (as long as you have a license), 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 many of the features on the GUI. 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	<p>To open the <b>Help</b> window:</p> <ul style="list-style-type: none"> <li>• In the <b>Model Builder</b> or <b>Physics Builder</b> click a node or window and then press F1.</li> </ul>
Linux	<ul style="list-style-type: none"> <li>• On the main toolbar, click the <b>Help</b> (  ) button.</li> <li>• From the main menu, select <b>Help&gt;Help</b>.</li> </ul>

### Opening the Documentation Window

Win	<p>To open the <b>Documentation</b> window:</p> <ul style="list-style-type: none"> <li>• Press Ctrl+F1.</li> <li>• From the <b>File</b> menu select <b>Help&gt;Documentation</b> (  ).</li> </ul>
-----	--

Mac	<p>To open the <b>Documentation</b> window:</p> <ul style="list-style-type: none"> <li>• Press Ctrl+F1.</li> </ul>
Linux	<ul style="list-style-type: none"> <li>• On the main toolbar, click the <b>Documentation</b> (  ) button.</li> <li>• From the main menu, select <b>Help&gt;Documentation</b>.</li> </ul>

### THE APPLICATION LIBRARIES WINDOW

Each application includes documentation with the theoretical background and step-by-step instructions to create a model application. The applications are available in COMSOL as MPH-files that you can open for further investigation. You can use the step-by-step instructions and the actual applications as a template for your own modeling and applications. In most models, SI units are used to describe the relevant properties, parameters, and dimensions in most examples, 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 application and its properties, including options to open it or a PDF document.

	<p><a href="#">The Application Libraries Window</a> in the <i>COMSOL Multiphysics Reference Manual</i>.</p>
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### Opening the Application Libraries Window

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

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	<ul style="list-style-type: none"><li>• From the <b>Home</b> toolbar, <b>Windows</b> menu, click (  ) <b>Applications Libraries</b>.</li><li>• From the <b>File</b> menu select <b>Application Libraries</b>.</li></ul> <p>To include the latest versions of model examples, from the <b>File&gt;Help</b> menu, select (  ) <b>Update COMSOL Application Library</b>.</p>
	Select <b>Application Libraries</b> from the main <b>File&gt;</b> or <b>Windows&gt;</b> menus.
	To include the latest versions of model examples, from the <b>Help</b> menu select (  ) <b>Update COMSOL Application Library</b> .

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### CONTACTING COMSOL BY EMAIL

For general product information, contact COMSOL at [info@comsol.com](mailto:info@comsol.com).

To receive technical support from COMSOL for the COMSOL products, please contact your local COMSOL representative or send your questions to [support@comsol.com](mailto:support@comsol.com). An automatic notification and a case number are sent to you by email.

### COMSOL ONLINE RESOURCES

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Support Knowledge Base	<a href="http://www.comsol.com/support/knowledgebase">www.comsol.com/support/knowledgebase</a>

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# Overview of the User's Guide

The *Electrochemistry 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](#).

## ELECTROCHEMISTRY INTERFACES

[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.

## CHEMICAL SPECIES TRANSPORT INTERFACES

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

## FLUID FLOW INTERFACES

[Fluid Flow Interfaces](#) chapter describes the Darcy's Law, Free and Porous Media Flow, and the Brinkman Equations interfaces, including the underlying theory for each.

## **HEAT TRANSFER INTERFACES**

[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 flow, potential, and temperature couplings, for example.



# Modeling with Electrochemistry

In this chapter you are given an [Introduction to Electrochemistry Modeling](#).

# Introduction to Electrochemistry Modeling

In this section:

- [What is Electrochemistry?](#)
- [Electrochemical Applications](#)
- [Fundamentals of Electrochemistry Modeling](#)
- [Current Distribution Cases and Choosing the Right Interface to Model an Electrochemical Cell](#)
- [Understanding the Different Approximations for Conservation of Charge in Electrolytes](#)
- [Modeling Electrochemical Reactions](#)
- [Double Layer Capacitance](#)
- [Porous Electrodes](#)
- [Boundary Conditions for Running and Controlling Electrochemical Cells](#)
- [Modeling Cyclic Voltammetry](#)
- [Common Simplifications when Modeling Electrochemical Cells](#)
- [Before You Start Building Your Model](#)
- [Meshing Advice](#)
- [Solving Electrochemical Models](#)
- [Postprocessing Your Solution](#)

## *What is Electrochemistry?*

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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*

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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*

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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.

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.



- [Potential Variables](#)
  - [Current Variables and Calculating the Total Cell Current](#)
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### *Current Distribution Cases and Choosing the Right Interface to Model an Electrochemical Cell*

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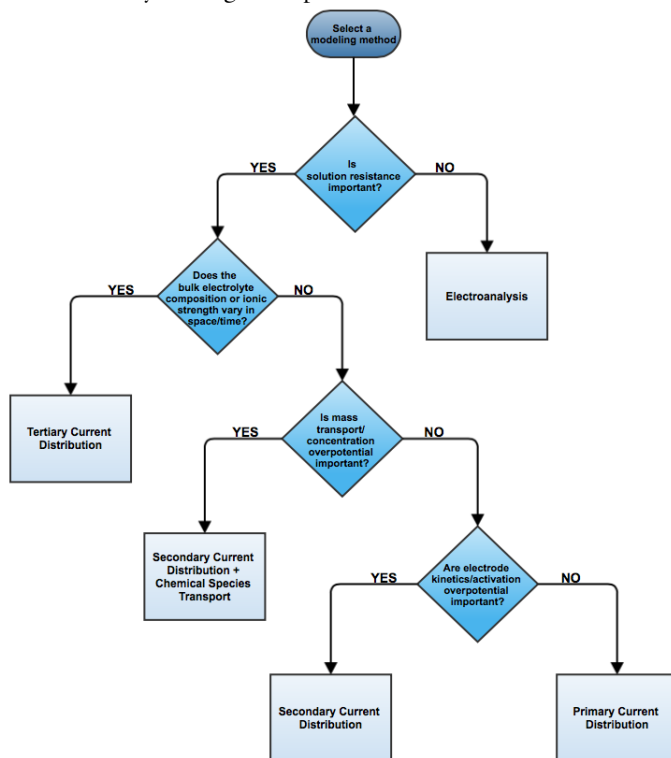
COMSOL Multiphysics has many built-in physics interfaces aimed at specific applications. In many generic cases, however, the modeler has to make some basic assumptions about his system before starting to build his model.

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 flow chart for selecting a proper current distribution interface for a model is shown below. The recommendations here are indicative and the modeler may sometimes wish 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 flow chart 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.



- [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:

$$x_D = \sqrt{\frac{RT \epsilon_0 \epsilon_s}{F^2 I}}$$

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



[The Tertiary Current Distribution, Nernst-Planck Interface](#)



The current flow itself is given by:

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

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

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

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

Clearly, the right-most term is zero: that is, convection of an electroneutral solution does not cause current flow. The left-most 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  $\sigma_l$  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:

$$\sigma_l \approx \frac{2F^2 ID_{\text{mean}}}{RT}$$

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  $\sigma_l$  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.

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Theory for the Current Distribution Interfaces

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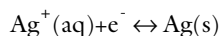
### *Modeling Electrochemical Reactions*

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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:



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:

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

where  $E_{\text{eq}, m}$  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

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

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:

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

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.



$\eta$  depends on both the electric potential in the electrode  $\phi_s$  and the electrolyte potential  $\phi_l$ . Where there is substantial resistance to current flow through a solution, the corresponding potential difference in  $\phi_l$ , 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 ( $i_0 \rightarrow \infty$ ) 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 ( $\eta$  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.
	<a href="#">Electrode Kinetics Expressions</a>

### 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-Electrolyte Interface 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:

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

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 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



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

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

where  $k_{\text{fwd}}$  and  $k_{\text{rwd}}$  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

$$E = \phi_s - \phi_l \quad (2-3)$$

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

$$\alpha_a + \alpha_c = n \quad (2-4)$$

By defining an equilibrium potential at which the forward reaction and backwards reaction rates are equal, [Equation 2-1](#) can be shown to be equivalent to the commonly used Butler-Volmer equation:

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

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

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

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

The overpotential is here defined as

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

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

$$E_{\text{eq}} = E_{\text{eq},0} - \frac{RT}{nF} \ln \frac{c_R}{c_O} \quad (2-8)$$

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

Note that in Equation 2-5 both  $i_0$  and  $E_{\text{eq}}$  are concentration dependent. This has some numerical drawbacks when modeling electrochemical cells including mass transport, since for low concentrations of the participating species, i.e. 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  $c_{R,\text{ref}}$  and  $c_{O,\text{ref}}$  (typically corresponding to the inlet or initial concentrations), resulting in

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

where

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

and

$$\eta = E - E_{\text{eq,ref}} \quad (2-11)$$

with



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

Note that [Equation 2-9](#) now contains a linear dependence on the activities  $c_O$  and  $c_R$ .

### *Double Layer Capacitance*

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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  $i_{\text{NF}} = dQ/dt$ . The total current recorded in a real experiment equals:

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

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.
	<a href="#">Porous Electrode Theory</a>

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### *Boundary Conditions for Running and Controlling Electrochemical Cells*

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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** vs ground to control the cell potential, or the **Electrode Potential** vs 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*

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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*

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#### **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-Electrolyte Boundary Interface

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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

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#### **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*

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#### *Before You Start Building Your Model*

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#### **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*

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

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

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

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

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



Meshing in the *COMSOL Multiphysics Reference Manual*

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## *Solving Electrochemical Models*

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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.
- 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. Usually ground should be set at the boundary with the fastest kinetics: for instance, the hydrogen electrode in a PEM fuel cell. 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 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 towards 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  $\max(c, \text{eps}^2)$ , 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.



- [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*:

- [Studies and Solvers](#)
- [Analyzing Model Convergence and Accuracy](#)
- [Achieving Convergence When Solving Nonlinear Equations](#)

### TIME-DEPENDENT PROBLEMS WITH LOAD STEPS

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

- Use smoothed current or potential load functions in order to avoid instantaneous or discrete load steps.
- Add a double layer capacitance to the model, which can improve the numerical stability.
- Reduce the **Maximum step** taken by the solver if you want to prevent the solver from “missing” short square load steps, or change the **Steps taken by solver** setting from **Free** to **Strict**, or **Intermediate**, to control the time steps using the **Times** text field. Using the Events interface can also be an option in certain cases if the load cycle itself varies dynamically.



- [Double Layer Capacitance](#)

In the *COMSOL Multiphysics Reference Manual*:

- [Step and Time Dependent](#)
  - [Building a COMSOL Multiphysics Model](#) and [The Events Interface](#)
- 

### SOLVER SETTINGS





Try adjusting the solver settings.

- In rare cases, try to increase the **Maximum number of iterations**.
- If you know the order of magnitude of the dependent variables beforehand, setting the scaling method to **Manual** for these can improve convergence and the accuracy of the results. This may be of special importance when solving for concentrations that are initially very small but where the final order of magnitude is known *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](#)
-

	<a href="#">Electrochemistry Studies and Study Steps and Cyclic Voltammetry</a> in the <i>COMSOL Multiphysics Reference Manual</i>
	In multi-component systems it is rarely straightforward to predict the rest potential and direction of current flow. The <b>Current Initialization</b> 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.
	<a href="#">Electrochemistry Studies and Study Steps</a> in the <i>COMSOL Multiphysics Reference Manual</i>
	<a href="#">Studies and Solvers and Building a COMSOL Multiphysics Model</a> in the <i>COMSOL Multiphysics Reference Manual</i>

### *Postprocessing Your Solution*

#### **POTENTIAL VARIABLES**

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

TABLE 2-1: 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

TABLE 2-1: COMMON POTENTIAL VARIABLES

VARIABLE	DESCRIPTION	DEFINED AT
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 **siec** 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, since 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.nll	A/m <sup>2</sup>	Electrolyte current density in normal direction	Boundaries to Electrolyte and Porous Electrode domains
xxx.nls	A/m <sup>2</sup>	Electrode current density in normal direction	Boundaries to Electrolyte and Porous Electrode domains
xxx.iloc_yy	A/m <sup>2</sup>	Local current density of electrode reaction	Electrode Reaction boundaries
xxx.itot	A/m <sup>2</sup>	Total interface current density (local sum of all xxx.iloc_yy)	Electrode Reaction boundaries
xxx.iv_yy	A/m <sup>3</sup>	Volumetric current density of a Porous Electrode Reaction	Porous Electrode domains
xxx.ivtot	A/m <sup>3</sup>	Total volumetric current densities (local sum of all xxx.iv_yy)	Porous Electrode domains
xxx.lIMag	A/m <sup>2</sup>	Electrolyte current density magnitude (L <sup>2</sup> norm)	Electrolyte domains
xxx.lSMag	A/m <sup>2</sup>	Electrode current density magnitude (L <sup>2</sup> norm)	Electrode domains



xxx denotes the tag of the physics interface. For instance **siec** 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** component 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.

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	In the <i>COMSOL Multiphysics Reference Manual</i> : <ul style="list-style-type: none"><li>• <a href="#">Component Couplings and Coupling Operators</a> and <a href="#">Integration</a></li></ul>
	Avoid evaluating the xxx.lIMag/xxx.lIMag variables on boundaries. These are generally less accurate than the xxx.nll/xxx.nls variables.

---

# Electrochemistry Interfaces

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

In this chapter:

- [The Primary and Secondary Current Distribution Interfaces](#)
- [The Tertiary Current Distribution, Nernst-Planck Interface](#)
- [Shared Physics Features in the Current Distribution Interfaces](#)
- [The Electrode, Shell Interface](#)
- [The Electroanalysis Interface](#)
- [Theory for the Current Distribution Interfaces](#)
- [Theory for Electrochemical Heat Sources](#)
- [Theory for the Electrode, Shell Interface](#)
- [Theory for the Electroanalysis Interface](#)
- [Electrode Potentials and Reference Electrodes](#)

# 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](#)
- [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](#)






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

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## *The Primary Current Distribution and Secondary Current Distribution Interfaces*

The **Primary Current Distribution (siec)** interface () and the **Secondary Current Distribution (siec)** 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.

#### **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 `siec`.

#### **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, amongst 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.

## DISCRETIZATION

To display this section, click the **Show** button (  ) and select **Discretization**.



- [Electrochemical Reactions and the Difference Between a Primary and a Secondary Current Distribution](#)
- [Domain Equations for Primary and Secondary Current Distributions](#)
- [Shared Physics Features in the Current Distribution Interfaces](#)
- [Theory for the Current Distribution Interfaces](#)



Secondary Current Distribution: *Wire Electrode*: Application Library path **Electrochemistry\_Module/Electrochemical\_Engineering/wire\_electrode**

### *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**,  $\sigma_l$  (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 non-linear 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*

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The **Porous Electrode** node sets up charge balances for the electrode and the pore electrolyte in a porous electrode. 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.

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.

Note that the **Porous Electrode** 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.

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).

#### **FILM RESISTANCE**

See the [Electrode Surface](#) node.



- [Domain Equations for Primary and Secondary Current Distributions](#)
  - [Porous Electrode Theory](#)
- 

### *Periodic Condition*

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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*.

## Edge Electrode

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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.

### 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** button (  ) and select **Advanced Physics Options**.



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.

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### *Electrode Line Current Source*

---



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



For 2D components use it on points.



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

---

#### **ELECTRODE CURRENT SOURCE**

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

### *Electrolyte Line Current Source*

---



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



For 2D components use it on points.



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

---

#### **ELECTROLYTE CURRENT SOURCE**

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

### *Electrode Symmetry Axis Current Source*

---



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

---

#### **ELECTRODE CURRENT SOURCE**

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

### *Electrolyte Symmetry Axis Current Source*

---



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

---

#### **ELECTROLYTE CURRENT SOURCE**

Enter the **Electrolyte current source**  $q_{1,l}$  (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.

# The Tertiary Current Distribution, Nernst-Planck Interface

In this section:

- [The Tertiary Current Distribution, Nernst-Planck Interface](#)
- [Electrolyte](#)
- [Porous Electrode](#)
- [Separator](#)
- [Reactions](#)
- [Initial Values](#)

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





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All other nodes in the Tertiary Current Distribution, Nernst-Planck interface are described in [Shared Physics Features in the Current Distribution Interfaces](#)

---

## *The Tertiary Current Distribution, Nernst-Planck Interface*

The **Tertiary Current Distribution, Nernst-Planck (tcdee)** 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 [Charge Conservation model](#) 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.



## 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 `tcdee`.

## 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:  $\text{m}^2$ ) to define a parameter for the area of the geometry perpendicular to the 1D component. The value of this parameter is used, amongst other things, to automatically calculate the total current from the current density vector. The analogy is valid for other fluxes. The default is  $1 \text{ m}^2$ .

## CHARGE CONSERVATION MODEL

The physics interface features four 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.

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

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 **Concentrations** of the species, the **Electrolyte potential**, and the **Electric potential**.


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

#### **DISCRETIZATION**

To display this section, click the **Show** button (  ) and select **Discretization**.

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

#### **CONSISTENT STABILIZATION AND INCONSISTENT STABILIZATION**

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

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

- When the **Crosswind diffusion** check box is selected, a weak term that reduces spurious oscillations is added to the transport equation. The resulting system is nonlinear. There are two options for **Crosswind diffusion type**:
  - **Do Carmo and Galeão**—the default option. This type of crosswind diffusion reduces undershoot and overshoot to a minimum but can in rare cases give equations systems that are difficult to fully converge.
  - **Codina**. This option is less diffusive compared to the Do Carmo and Galeão option but can result in more undershoot and overshoot. It is also less effective for anisotropic meshes. The Codina option activates a text field for the **Lower gradient limit**  $g_{lim}$  (SI unit: mol/m<sup>4</sup>). 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 2-3](#) for links to common sections and [Table 2-4](#) to common feature nodes. You can also search for information: press F1 to open the **Help** window or Ctrl+F1 to open the **Documentation** window.



- [The Nernst-Planck Equations](#)
- [Domain Equations for Tertiary Current Distributions Using the Nernst-Planck Equations and Electroneutrality](#)
- [Shared Physics Features in the Current Distribution Interfaces](#)
- [Theory for the Current Distribution Interfaces](#)

### *Electrolyte*

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

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

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

By default the **Mobility** (SI unit: s·mol/kg) for each species is set to be calculated based on the **Diffusion coefficients** (SI unit:  $m^2/s$ ) 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](#)
- 

### *Porous Electrode*

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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. 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.

Correction factors may be used 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.

Note that the **Porous Electrode** 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.

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

## FILM RESISTANCE

See the [Electrode Surface](#) node



- [Porous Electrode Theory](#)
- [Porous Electrode Reactions Theory](#)
- [Domain Equations for Tertiary Current Distributions Using the Nernst-Planck Equations and Electroneutrality](#)

## *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  $R_{e2}$  (SI unit: mol/m<sup>3</sup>·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 non-porous 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  $\epsilon_l$ . ( $\epsilon_l$  equals unity for non-porous 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 non-linear 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 non-zero 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 Boundary*

---

Use the ion exchange membrane boundary node to specify a 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 problems.

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 non-zero charge number). Use the **Membrane potential** setting to set the electrolyte potential on the membrane side of the boundary. Note: 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**.



- Ion Exchange Membrane Boundary Theory
-

# Shared Physics Features in the Current Distribution Interfaces

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

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[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
- Insulation
- Internal Electrode Surface
- Line Mass Source<sup>1</sup>
- Point Mass Source<sup>1</sup>
- Porous Electrode Reaction
- Porous Electrode Reaction
- Porous Matrix Double Layer Capacitance
- Reference Electrode
- Symmetry

<sup>1</sup> 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 2-3](#) for links to common sections and [Table 2-4](#) 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**  $\sigma_s$  (SI unit: S/m) parameter will define how the current in the domain depends on the gradient of the potential.



## 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<sup>3</sup>), is added according to the following equation:

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

where

$$\mathbf{i}_s = -\sigma_s \nabla \phi_s$$

and  $\sigma_s$  denotes the electrode's conductivity and  $\phi_s$  the electric potential.

To use this feature, click the **Show** button (  ) and select **Advanced Physics Options** 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<sup>3</sup>), is added according to the following equation:

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

To use this feature, click the **Show** button (  ) and select **Advanced Physics Options** 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 and Stoichiometric Coefficients sections.

### **ACTIVE SPECIFIC SURFACE AREA**

The **Active specific surface area**,  $a_v$  (SI unit:  $\text{m}^2/\text{m}^3$ ) specifies the area of the electrode-electrolyte interface that is catalytically active for this porous electrode reaction.  $a_v$  is multiplied by  $i_{\text{loc}}$ , 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**  $C_{\text{dl}}$  (SI unit:  $\text{F}/(\text{m}^2)$ ) and the **Double layer area**  $a_{v,\text{dl}}$  (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.

## *Insulation*

---

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

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

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

### *Symmetry*

---

For the Primary Current Distribution and Secondary Current Distribution interfaces, the **Symmetry** boundary condition is identical to the [Insulation](#) condition.

For the Tertiary Current Distribution, Nernst-Planck interface, the **Symmetry** boundary condition imposes a no flux condition for the molar flux of species at a boundary.



### Symmetry Theory

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### *Electrode Surface*

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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 internal boundaries between electrolyte and electrode domains, use the [Internal Electrode Surface](#) node.

#### **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**  $R_{\text{film}}$  (SI unit:  $\Omega \cdot \text{m}^2$ ) 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.

**Electric potential** and **Electrode potential** will set the potential value directly, whereas **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 [External Short](#) node for further information about this boundary condition.

## 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** button (  ) and select **Advanced Physics Options**.



- [Electrode Reactions Theory](#)
- [Film Resistance](#)

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### *Electrode Reaction*

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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 the Electrode Kinetics and Stoichiometric Coefficients sections described below are not available for all Electrochemistry interfaces.

#### **EQUILIBRIUM POTENTIAL**

The **Equilibrium potential**,  $E_{\text{eq}}$  (SI unit: V), is used in the electrode kinetics expressions in the following section (via the definition of the over potential), or for setting up primary current distribution potential constraints.

The **Temperature derivative of equilibrium potential parameter**,  $dE_{\text{eq}}/dT$  (SI unit: V/K), is used when calculating the reversible heat source of the electrode reaction, which in turn can be used for coupling to heat transfer physics. Note that  $dE_{\text{eq}}/dT$  parameter value has no impact on the equilibrium potential variable.

#### **ELECTRODE KINETICS**

The settings of this section will define the **Local current density**,  $i_{\text{loc}}$  (SI unit:  $\text{A}/\text{m}^2$ ), at the interface between the electrolyte and the electrode. Note that  $i_{\text{loc}}$  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:  $\text{A}/\text{m}^2$ ) is a measure of the kinetic activity.

#### *Butler-Volmer or Linearized Butler-Volmer*

These kinetics expression are typically used for secondary current distribution problems.

The **Linearized Butler-Volmer** is valid when the overpotentials of the reactions are small ( $\ll 25$  mV). The linearized version can also be used to troubleshoot a model with convergence problems.

The **Anodic transfer coefficient**,  $\alpha_a$  (dimensionless), and **Cathodic transfer coefficient**,  $\alpha_c$  (dimensionless), parameters will impact how much  $i_{loc}$  will change upon changes in the overpotential.

#### *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 ( $\gg 100$  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 ( $\ll -100$  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 kinetics expression type is typically used in 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.

#### *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.

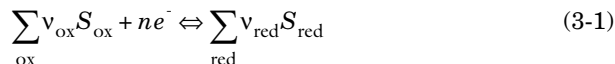
#### *Limiting Current Density*

Use the **Limiting Current Density** 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  $i_{\text{lim}}$  (SI unit: A/m<sup>2</sup>).

#### **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:



Set  $v_j$  as positive ( $v_{\text{red}}$ ) for the reduced species and negative ( $v_{\text{ox}}$ ) for the oxidized species in an electrochemical reaction. The number of participating electrons,  $n$ , should be positive.



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.



- [Electrode Reactions Theory](#)
- [Electrode Kinetics Expressions](#)

#### *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.

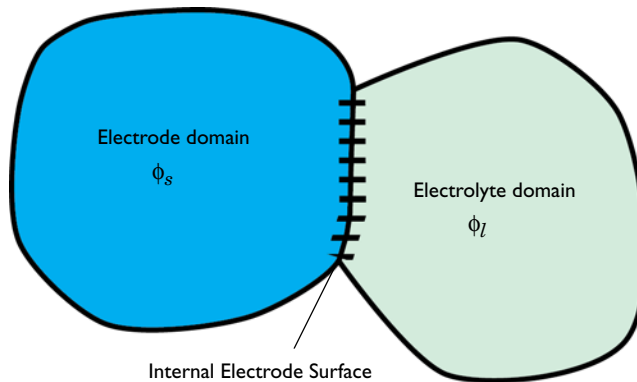
The parent node may be either an [Internal Electrode Surface](#) or a [Electrode Surface](#).

This subnode is not available for the Primary Current Distribution interface.

### *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 internal 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 and Constraint Settings sections, see the [Electrode Surface](#) node.



- [Electrode Reactions Theory](#)

## *Electrolyte Potential*

---

Add the **Electrolyte Potential** node from **Electrolyte** submenus for boundaries, edges, and points to set a fixed potential at a position in the electrolyte. This node can be used to model half-cells, or to set the electrolyte potential at the position of, for example, a reference electrode.

The node sets the potential in the electrolyte,  $\phi_l$ , 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** button () and select **Advanced Physics Options**.

## *Electrolyte Current*

---

The **Electrolyte Current** boundary condition sets the total current or average current density of a boundary. 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** button () and select **Advanced Physics Options**.



- [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.

### *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** button (  ) on the **Model Builder** and then select **Advanced Physics Options** then add the **Electrode-Electrolyte Boundary Interface** node from the **Electrode** or **Pairs>Electrode** submenu.

Use this node to model an electrochemical interface between an electrolyte and an electrode where the electrolyte domain is not included explicitly in the model. The node can only be applied on outer boundaries to electrode domains. Set the potential of the electrolyte either explicitly, or specify a current condition that the potential of the electrode shall fulfill.

[Electrode Reaction](#) and [Double Layer Capacitance](#) subnodes are available from the context menu (right-click the parent node) or from the **Physics** toolbar, **Attributes** menu.

This node is available for the Secondary Current Distribution and Tertiary Current Distribution, Nernst-Planck interfaces.

#### **BOUNDARY CONDITION**

This section specifies the potential of the electrolyte phase for the electrolyte-electrode interface. The electrolyte potential is used (via the overpotential) by the **Electrode Reaction** subnodes.

The **Electrolyte potential** will set the potential value directly, whereas **Total current** or **Average current density** both add an extra global degree of freedom for the potential in the electrolyte phase, set to comply with the chosen condition.

When using the **Total current** option in 1D or 2D, the boundary area is based either on the **Cross sectional area** (1D) or the **Out-of-Plane thickness** (2D) properties, set on the physics interface top node.

## *Electric Ground*

---

This node 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** button (  ) and select **Advanced Physics Options**.

## *Electric Potential*

---

This node sets the electric potential in the electrode (or a porous electrode),  $\phi_s$ , to a value,  $\phi_{s, \text{bnd}}$  according to the following:

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

The node is typically used to set the cell voltage at 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** button (  ) and select **Advanced Physics Options**.

## *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 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** button (  ) and select **Advanced Physics Options**



- [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.



- [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.



[Harmonic Perturbation, Prestressed Analysis, and Small-Signal Analysis](#)  
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** button (  ) and select **Advanced Physics Options**.



[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:

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

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

## *Reference Electrode*

---

The **Reference Electrode** node is a point feature applicable to electrolyte domains. It defines a global electric reference potential and can be used in the [Electrode Potential](#) node for setting the electric potential of an electrode boundary with respect to the reference potential.

### **EQUILIBRIUM POTENTIAL**

See [Electrode Reaction](#) for information about the settings of this section.



[Electrode Potentials and Reference Electrodes](#)

---

## *Electric Reference Potential*

---

The **Electric Reference Potential** node is a point feature applicable to electrode domains. It defines a global electric reference potential equal to the electric potential in the point and can be used in the [Electrode Potential](#) feature for setting the electric potential of an electrode boundary with respect to the reference potential.



[Electrode Potentials and Reference Electrodes](#)

---



## *Circuit Terminal*

---

This feature is only available with an AC/DC Module license.

Use the **Circuit Terminal** node to specify a coupling to the **External IvsU** node in the **Electrical Circuit** interface.

# The Electrode, Shell Interface

The **Electrode, Shell (els)** interface () , found under the **Electrochemistry** branch () when adding a physics interface, models electric current conduction in the tangential direction on a boundary.

The physics interface is suitable for modeling thin electrodes where the potential variation in the normal direction to the electrode is negligible. This assumption allows for the thin electrode domain to be replaced by a partial differential equation formulation on the boundary. In this way the problem size can be reduced, and potential problems with mesh anisotropy in the thin layer can be avoided.

Ohm's law is used in combination with a charge balance to describe the conduction of currents in the shell electrode.

When this physics interface is added, these default nodes are also added to the **Model Builder**— **Electrode**, **Electric Insulation** (the default edge or point condition), and **Initial Values**. Then, from the **Physics** toolbar, add other nodes that implement, for example, edge or point conditions and current sources. You can also right-click **Electrode, Shell** to select physics features from the context menu.

## SETTINGS

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

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

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

## THICKNESS



---

For 2D components, enter a value or expression for the **Out-of-plane thickness**  $d$  (SI unit: m). The default value is 1 m.


---



## DEPENDENT VARIABLES

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 display this section, click the **Show** button () and select **Discretization**.



- [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 2-3](#) for links to common sections and [Table 2-4](#) to common feature nodes. You can also search for information: press F1 to open the **Help** window or Ctrl+F1 to open the **Documentation** window.

---

### *Boundary, Edge, Point, and Pair Nodes for the Electrode, Shell Interface*

---

[The Electrode, Shell Interface](#) has these boundary, edge, point, and pair nodes, listed in alphabetical order, available from the **Physics** ribbon toolbar (Windows users), **Physics** context menu (Mac or Linux users), or right-click to access the context menu (all users).

---



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

---

These physics nodes are described in this section:

- [Boundary Current Source](#)
- [Current Source](#)
- [Electrode](#)
- [Electric Insulation](#)
- [Electric Potential](#)
- [External Current Density](#)
- [Ground](#)
- [Initial Values](#)
- [Normal Current Density](#)

These nodes are available and described for the Current Distribution interfaces, where edges (3D components) or points (2D and 2D axisymmetric components) are selected instead of boundaries.

- [Electrode Potential](#)
- [Electric Reference Potential](#)



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



In the *COMSOL Multiphysics Reference Manual* see [Table 2-3](#) for links to common sections and [Table 2-4](#) 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**  $\sigma$  (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 **Anisotropic** 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.



### *Initial Values*

---

The **Initial Values** node adds the electric potential that can serve as an initial guess for a nonlinear solver. If more than one initial value is needed, add **Initial Values** nodes from the **Physics** toolbar.

#### **INITIAL VALUES**

Enter values or expressions for the **Electric potential** (SI unit: V). The default value is 0 V.

### *External Current Density*

---

Use the **External Current Density** node to define the external current density.

#### **EXTERNAL CURRENT DENSITY**

Based on space dimension, enter the vector components (**x**, **y**, and **z** for 3D components, **x** and **y** for 2D, or **r** and **z** for 2D axisymmetric components) of the **External current density**  $\mathbf{i}_e$  (SI unit: A/m<sup>2</sup>). The defaults are 0 A/m<sup>2</sup>.

### *Current Source*

---

The **Current Source** node adds a source term to [Equation 3-3](#). 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<sup>3</sup>). The default is 0 A/m<sup>3</sup>.

### *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<sup>2</sup>). The default is 0 A/m<sup>2</sup>.

### *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<sup>2</sup>). The default is 0 A/m<sup>2</sup>.

### *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** button (  ) and select **Advanced Physics Options**.

### *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** button (  ) and select **Advanced Physics Options**.

# The Electroanalysis Interface

The **Electroanalysis (elan)** interface () , found under the **Electrochemistry** branch () when adding a physics interface, has the equations, boundary conditions, and rate expression terms for modeling mass transport of diluted species in electrolytes using the diffusion-convection equation, solving for electroactive species concentration(s). The physics interface contains tailor-made functionality for modeling cyclic voltammetry and electrochemical impedance spectroscopy.

Use this physics interface to model electroanalytical problems with electrolyte solutions containing a large quantity of inert “supporting” electrolyte. Ohmic loss is assumed to be negligible.

The settings for this physics interface can be chosen so as to simulate chemical species transport through diffusion (Fick’s law), migration (when coupled to an electric field—electrokinetic flow), and convection (when coupled to fluid flow).

The physics 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 default dependent variables are the molar concentrations,  $c_1$  and  $c_2$ , of the two electroactive species in a redox couple

Note that most of the physics interface settings are the same as for [The Transport of Diluted Species 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 `elan`.

## 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, the **Cross sectional area** field (default value:  $1 \text{ m}^2$ ) defines 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.

### TRANSPORT MECHANISMS

Diffusion is always included. By default, the **Convection** and **Migration in electric field** check boxes are not selected under **Additional transport mechanisms**.

- Selecting the **Convection** check box enables the addition of the **Inflow** and **Outflow** boundary nodes.
- Selecting the **Migration in electric field** check box activates the migration transport of ionic species in the [Transport Properties](#) node. Since supporting electrolytes of high conductivity are usually used in electroanalytical problems, migrative effects are usually negligible.

	The physics interface has one tailor-made study type, see <a href="#">Cyclic Voltammetry</a> in the <i>COMSOL Multiphysics Reference Manual</i> .
	<i>Cyclic Voltammetry at a Macroelectrode in 1D</i> Application Library path: <b>Electrochemistry_Module/Tutorials/cyclic_voltammetry_1d</b>
	<ul style="list-style-type: none"> <li>• <a href="#">Theory for the Electroanalysis Interface</a></li> <li>• <a href="#">Domain, Boundary, and Pair Nodes for the Electroanalysis Interface</a></li> </ul>
	In the <i>COMSOL Multiphysics Reference Manual</i> see <a href="#">Table 2-3</a> for links to common sections and <a href="#">Table 2-4</a> to common feature nodes. You can also search for information: press F1 to open the <b>Help</b> window or Ctrl+F1 to open the <b>Documentation</b> window.

### *Domain, Boundary, and Pair Nodes for the Electroanalysis Interface*

The [Electroanalysis Interface](#) has these domain, boundary, and pair nodes available, 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.

---



A boundary pair occurs when the solutions on two separate surfaces within a simulation are related (such as when two components in an assembly are touching)

---

These nodes are described in this section:

- [Transport Properties](#)
- [Electrode Surface in the Electroanalysis Interface](#)
- [Electrode Reaction](#)
- [Initial Values](#)




These nodes are shared with and described for the Transport of Diluted Species interface (listed in alphabetical order):

- Concentration
- Electrode-Electrolyte Interface Coupling
- Equilibrium Reaction
- Flux
- Flux Discontinuity
- Double Layer Capacitance<sup>1</sup>
- Inflow<sup>2</sup>
- No Flux
- Open Boundary
- Outflow
- Periodic Condition
- Porous Electrode Coupling
- Reaction Coefficients
- Reactions
- Symmetry
- Thin Diffusion Barrier

<sup>1</sup>This is documented for the Current Distribution interfaces

<sup>2</sup>This is available when the **Convection** check box is selected on the physics interface **Settings** window.



Some of the above nodes require that you click the **Show** button (  ) and select **Advanced Physics Options** to enable the option in the context menu. This requirement is for **Flux Discontinuity**, **Periodic Condition**, **Thin Diffusion Barrier**, **Electrode-Electrolyte Interface Coupling**, **Porous Electrode Coupling**, and **Reaction Coefficients**.



In the *COMSOL Multiphysics Reference Manual* see [Table 2-3](#) for links to common sections and [Table 2-4](#) 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.

### *Transport Properties*

This node defines the transport properties of the electrolyte. What settings are available is dependent on the transport mechanisms that have been chosen in the Electroanalysis interface topnode (any combination of convection, migration, and diffusion), and includes only the input fields required by the activated transport mechanisms.

## MODEL INPUTS

The **Temperature** is **User defined** by default. If a Heat Transfer interface is included in the model, alternatively select the temperature for that interface. For example, if a Heat Transfer in Fluids interface is included in the model, the **Temperature (ht)** option is available.

## CONVECTION

This section is available when the **Convection** check box is selected on the interface top node. The **Velocity field  $\mathbf{u}$**  (SI unit: m/s) of the solvent is specified as a feature input. The default is **User defined**, but if a Fluid Flow interface is included in the model, you may select the velocity field for that physics interface. For example, if a Laminar Flow interface is included in the model, the **Velocity field (spf)** option is available from the list.

## DIFFUSION

Enter the **Diffusion coefficient  $D_c$**  manually, or use a value from the **Materials** node. The default **Diffusion coefficient** value is  $1\text{e-}9\text{ m}^2/\text{s}$  which is a typical order of magnitude for a species diluted in a liquid aqueous solution.

## MIGRATION IN ELECTRIC FIELD

You may include Migration by enabling the **Migration in electric field** check box on the Electroanalysis top node.

Choose the source for where the **Electrolyte potential  $\phi_l$**  (SI unit: V). Note that the migration term in the transport equation is based on the gradient of the electrolyte potential. If there is no spatial variation in  $\phi_l$ , the migration term will be zero.

By default the **Mobility** (s·mol/kg) is set to be calculated based on the species diffusivity and the temperature using the **Nernst-Einstein relation**.

Only species with a non-negative **Charge number  $z_c$**  (dimensionless, but requires a plus or minus sign) will be affected by the migrative transport.

## *Initial Values*

---

The **Initial Values** node adds the initial values for the concentration of each species to be specified. These serve as an initial guess for a stationary solver or as an initial condition for a transient simulation.

Add multiple **Initial Values** nodes with different domain selections to define different initial values in different domains.

Setting all the **Concentration** (SI unit: mol/m<sup>3</sup>) initial values to 0 may lead solver convergence problems, for instance in models using concentration dependent kinetics in an [Electrode Reaction](#) node. Using small positive values instead of 0 may mitigate such issues.

### *Electrode Surface in the Electroanalysis Interface*

---

The **Electrode Surface** node defines an electrode surface located on an external boundary to a [Transport Properties](#) (electrolyte) domain. The node will set up a flux boundary condition, based on electrode reaction current densities and stoichiometric coefficients according to Faraday's law of electrolysis.

By default, an [Electrode Reaction](#) subnode is added to the feature and an arbitrary number of these subnodes can be added, which contribute to the total flux over the boundary. You may also add a [Double Layer Capacitance](#) subnode.

The overpotential used by the **Electrode Reaction** subnode is based on the electric potential of the **Electrode Surface**, the electrolyte potential and the individual equilibrium potentials of the **Electrode Reaction** subnodes.

Use the **Boundary Condition** section to control the electric potential. The electrolyte potential is set to 0 by default. To use another value, enable **Migration Electric Field** on the **Electroanalysis** topnode, and set the value on the [Transport Properties](#) node. The **Film Resistance** section can also contribute to the overpotentials.

#### **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**  $R_{\text{film}}$  (SI unit:  $\Omega \cdot \text{m}^2$ ) 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.

This section is not available if **Counter electrode** is selected as the **Boundary condition**.

### BOUNDARY CONDITION

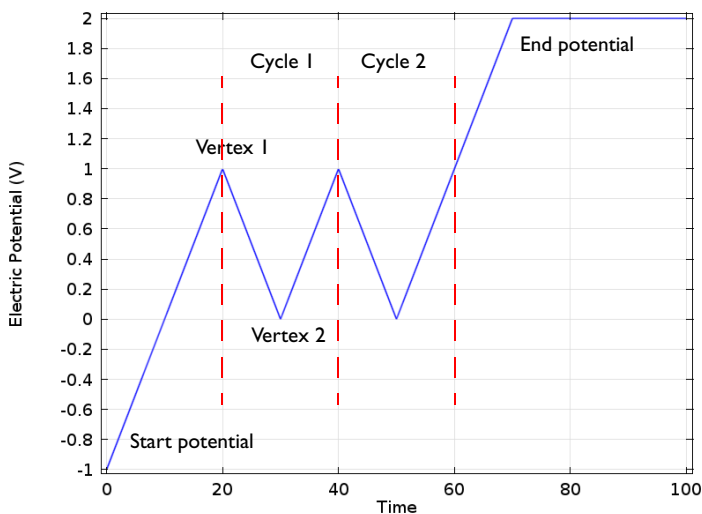
This section specifies the potential in the electrode phase of the electrolyte-electrode interface. The electrode potential is used (via the overpotential) by the **Electrode Reaction** subnodes.

**Electric potential**, **Electrode potential** and **Cyclic voltammetry** will set the potential value directly, whereas **Total current**, **Average current density** or **Counter electrode** all add an extra global degree of freedom for the potential in the electrode phase, set to comply with the chosen condition.

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.

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.


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.

### ADVANCED SETTINGS

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

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  $1 \cdot 10^{-3}$ . 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. .



- [Cyclic Voltammetry and Waveform](#) in the *COMSOL Multiphysics Reference Manual*
- [Theory for the Coupling of Mass Transport to Electrochemical Reactions](#)
- [Counter Electrodes and Overall Charge Balance](#)



*Cyclic Voltammetry at a Macroelectrode in 1D* Application Library  
path: **Electrochemistry\_Module/Tutorials/cyclic\_voltammetry\_1d**

### *Electrode Reaction*

The **Electrode Reaction** subnode defines the electrode kinetics for the charge transfer reaction that occurs between the electrolyte and the electrode on the surface of a non-porous electrode. A default node is added where the electrode kinetics can be set up for the charge transfer reaction. The **Electrode Reactions** subnode is added by default to the [Electrode Surface in the Electroanalysis Interface](#). You can also add it from the context menu (right-click the parent node) or from the **Physics** toolbar, **Attributes** menu.

### ELECTRODE KINETICS

Except for the **Electroanalytical Butler-Volmer** settings described below, see the [Electrode Reaction](#) node for information about the other settings.

The **Electroanalytical Butler-Volmer** is a concentration dependent kinetics expression based on a **Heterogenous rate constant**  $k_0$  (SI unit: m/s), the **Cathodic transfer coefficient**

$\alpha_c$  (dimensionless) and the reaction coefficients settings on the Stoichiometric Coefficients section by which  $c_{\text{red}}$  and  $c_{\text{ox}}$  are determined.



### The Electroanalytical Butler–Volmer Equation

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# Theory for the Current Distribution Interfaces

In this section:

- [The Nernst-Planck Equations](#)
- [Domain Equations for Primary and Secondary Current Distributions](#)
- [Electrochemical Reactions and the Difference Between a Primary and a Secondary Current Distribution](#)
- [Domain Equations for Tertiary Current Distributions Using the Nernst-Planck Equations and Electroneutrality](#)
- [Mass Fluxes and Sources Due to Electrochemical Reactions](#)
- [Film Resistance](#)
- [Electrode Kinetics Expressions](#)
- [Theory for Specific Current Distribution Feature Nodes](#)



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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.

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## *The Nernst-Planck Equations*

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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 flux of species  $i$  (SI unit: mol/(m<sup>2</sup>·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-hand side in the equation below.

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

where

- $c_i$  represents the concentration of the ion  $i$  (SI unit: mol/m<sup>3</sup>),
- $z_i$  its valence,
- $D_i$  the diffusion coefficient (SI unit: m<sup>2</sup>/s),
- $u_{m,i}$  its mobility (SI unit: s·mol/kg),
- $F$  denotes the Faraday constant (SI unit: C/mol),
- $\phi_i$  the electrolyte potential, and
- $\mathbf{u}$  the velocity vector (SI unit: m/s).

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<sup>2</sup>) in the electrolyte.

### *Domain Equations for Primary and Secondary Current Distributions*

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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,  $Q_b$ , 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*,  $\sigma_k$  denotes the conductivity (SI unit: S/m) and  $\phi_k$  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  $\eta_m$ , is the following:

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

where  $E_{\text{eq}, m}$  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,  $\eta_m$ , 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,  $E_{\text{eq}, m}$ . This condition is implemented as the following constraint on boundaries between electrodes and electrolyte domains:

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



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:

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

where  $i_{\text{loc}, m}$  denotes the local charge transfer current density for reaction  $m$ ,  $i_0$  the exchange current density,  $\alpha_a$  the anodic transfer coefficient,  $\alpha_c$  the cathodic charge transfer coefficient,  $F$  *Faraday's constant*, and  $R$  the universal gas constant.



It is possible to expand the expression above to include the dependence of kinetics on concentration.

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.

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### *Domain Equations for Tertiary Current Distributions Using the Nernst-Planck Equations and Electroneutrality*

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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:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i - z_i u_{m, i} F c_i \nabla \phi_l + c_i \mathbf{u}) = R_{i, tot}$$

where

- $c_i$  denotes the concentration of species  $i$  (SI unit: mol/ m<sup>3</sup>),
- $D_i$  the diffusion coefficient of species  $i$  (SI unit: m<sup>2</sup>/s),
- $z_i$  the charge number of the ionic species (dimensionless),

- $u_{m,i}$  the ionic mobility of a species  $i$  (SI unit: mol·s/kg),
- $F$  the Faraday constant (SI unit: C/mol), and
- $\phi_l$  denotes the electric potential (SI unit: V).

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

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



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,  $i_{loc}$  (SI unit: A/m<sup>2</sup>), which in this case can contain concentration dependencies:

$$i_{loc} = i_0 \left( \prod \left( \frac{c_i}{c_{i,ref}} \right)^{\gamma_{i,a}} \exp\left(\frac{\alpha_a F \eta}{RT}\right) - \prod \left( \frac{c_i}{c_{i,ref}} \right)^{\gamma_{i,c}} \exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right)$$

where  $i_0$  denotes the exchange current density (SI unit: A/m<sup>2</sup>),  $\alpha_a$  the anodic charge transfer coefficient (dimensionless),  $\alpha_c$  the cathodic charge transfer coefficient (dimensionless),  $\gamma_{i,a}$  the anodic reaction order for species  $i$  (dimensionless), and  $\gamma_{i,c}$  is the cathodic reaction order for species  $i$  (dimensionless). The overpotential,  $\eta$ , is defined as in preceding sections, according to the following equation:

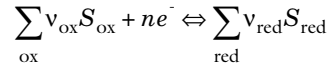
$$\eta = \phi_s - \phi_l - E_{eq}$$

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*

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When relating the species fluxes at an electrode surface to the electrical currents, the general electrochemical reaction formula:



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<sup>2</sup>·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<sup>2</sup>) 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:

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

where  $a_{v,m}$  (SI unit:  $\text{m}^2/\text{m}^3$ ) is the specific surface area.

### *Film Resistance*

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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  $R_{\text{film}}$  (SI unit:  $\text{ohm}\cdot\text{m}^2$ ) is a generalized film resistance and  $i_{\text{tot}}$  the sum of all currents over the interface. The activation overpotentials,  $\eta_m$ , for all occurring electrode reactions on the electrode with the film receive an extra potential contribution due to the film resistance according to:

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

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

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

where  $s_0$  is the reference/initial film thickness,  $\Delta s$  the electrode thickness change, and  $\sigma_{\text{film}}$  the conductivity (S/m) of the film.

## *Electrode Kinetics Expressions*

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A number of different analytical expressions for  $i_{loc,m}$  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  $\eta$ , is the following:

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

where  $E_{eq}$  denotes the equilibrium potential.

### *Butler-Volmer*

The most general expression is of Butler-Volmer type:

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

where  $\alpha_c$  denotes the cathodic charge transfer coefficient,  $\alpha_a$  the anodic charge transfer coefficient.

### *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:

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

where  $\alpha_c$  denotes the cathodic charge transfer coefficient,  $\alpha_a$  the anodic charge transfer coefficient,  $i_0$  the exchange current density, and  $\eta$  the overpotential.

### *Anodic and Cathodic Tafel Equations*

By assuming either high anodic or cathodic overpotentials for a given current (that is, slow kinetics or low  $i_0$ ), one of the terms in the original Butler-Volmer potentials can be neglected.

The anodic Tafel equation is implemented as follows:

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

where  $A_a$  (SI unit: V) is the so-called Tafel slope. The cathodic Tafel expression is according to:

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

to account for the negative sign of cathodic charge transfer reactions.  $A_c$  is also required to be negative.

#### *Concentration Dependent Kinetics*

The following expression describes a charge transfer reaction according to the full Butler-Volmer equation, where the anodic and cathodic terms of the current density expression depend on the local concentrations of the electroactive species at the electrode surface:

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

where  $C_R$  and  $C_O$  are dimensionless expressions, describing the dependence on the reduced and oxidized species in the reaction.

#### *Exchange Current Density and Rate Constants*

The exchange current density typically depends on the local concentrations of the reacting species. For instance, for a one electron redox couple, defining  $C_O = c_o / c_{\text{ref}}$ ,  $C_R = c_r / c_{\text{ref}}$ , and  $i_0 = k_0 F c_{\text{ref}}$ , the above expression 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.

#### *Limiting Current Density*

The steady-state rate of electrode reactions never exceeds 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 by a concentration dependent kinetics expression as described above.

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, the following kinetics expression can be derived:



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

where  $i_{\text{expr}}$  ( $\text{A}/\text{m}^2$ ) is the current density expression in the absence of mass transport limitations for the species, and  $i_{\text{lim}}$  ( $\text{A}/\text{m}^2$ ) is the limiting current density that corresponds to the maximum transport rate of the species. The derivation of this expression assumes either a strictly anodic or an cathodic reaction.

### *Theory for Specific Current Distribution Feature Nodes*

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#### **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 use 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 and the rate of this reaction is described by the Butler-Volmer equation, the domain equations are the following:

$$\begin{aligned}\nabla \cdot \mathbf{i}_l &= A_v \cdot \left( i_0 \left( \exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right) \right) \\ \nabla \cdot \mathbf{i}_s &= -A_v \cdot \left( i_0 \left( \exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right) \right)\end{aligned}$$

where  $A_v$  denotes the specific surface area (dimension  $L^2/L^3$ ), and  $\eta$  the overpotential according to

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

and  $E_{\text{eq}}$  denotes the equilibrium potential for the charge transfer reaction.

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 exemplar Butler-Volmer expression above is also included in the

material balances as a reaction term,  $\mathcal{R}_i$ , 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

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

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

where  $i_{loc, m}$  ( $A/m^2$ ) 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:

$$\nabla \cdot \mathbf{i}_l = \sum_m A_v i_{loc, m}$$

$$\nabla \cdot \mathbf{i}_s = -\sum_m A_v i_{loc, m}$$

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  $\sigma_s$  denotes the electrical conductivity and  $\phi_s$  the electrolyte potential.

### 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.



### Electrolyte Current Density

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### 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  $\sigma_s$  denotes the electrode conductivity and  $\phi_s$  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:

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

### 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  $\sigma_s$  denotes the electrode conductivity and  $\phi_s$  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:

$$\begin{aligned} \phi_s &= \phi_{s, \text{bnd}} \quad \text{on } \partial\Omega \\ \int_{\partial\Omega} (\phi_{s, \text{bnd}} - \phi_{s, \text{ground}}) (\mathbf{i}_s \cdot \mathbf{n}) dS &= P_{\text{total}} \end{aligned}$$

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

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

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

where  $P_{\text{avg}}$  is the average power density on the boundary, and  $A$  is the boundary area.



For a galvanic cell, such as a battery during discharge or a fuel cell, there is a maximum power level, beyond which a further current increase causes a lowered output power due to increasing voltage losses. A result of this is that there can be two existing solutions for the same power setting. In these cases the choice of initial values determines the final solution.



Electrode Power

## ION EXCHANGE MEMBRANE BOUNDARY THEORY

In an ion exchange membrane the concentration of charge carriers is fixed, whereas charge carrying species are free to move in a liquid electrolyte. To preserve continuity of the electrochemical potential over a boundary between an ion exchange membrane and a free electrolyte, a potential shift of the electrolyte potential arises if the ion concentrations in the two domains are different.

At the boundary between a liquid electrolyte phase and a ion-exchange membrane phase, denoted  $l$  and  $m$ , the Donnan potential,  $\Delta\phi$ (V), describes the relation between the concentration of a species,  $c_l$  and  $c_m$  (mol/m<sup>3</sup>), at each side of the boundary and the electrolyte potentials  $\phi_l$  and  $\phi_m$ :

$$\Delta\phi = \phi_l - \phi_m = \frac{RT}{zF} \ln\left(\frac{c_l}{c_m}\right)$$

where  $T$ (K) is the temperature,  $R$  (mol/(J K)) the molar gas constant,  $z$  the species charge and  $F$ (C/mol) is Faraday's constant.

The current densities  $\mathbf{I}_l$  and  $\mathbf{I}_m$  in the normal direction  $\mathbf{n}$  on each side of the boundary are equal so that the current density over the membrane-liquid interface is continuous:

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

The molar flux  $\mathbf{N}_l$  of the charge carrying species in the liquid electrolyte is set proportional to the current density according to Faraday's law:

$$\mathbf{n} \cdot \mathbf{N}_l = \frac{\mathbf{n} \cdot \mathbf{I}_l}{zF}$$

For all other species the molar flux is zero.

# Theory for Electrochemical Heat Sources

Heat sources and sinks appear in an electrochemical cell due to both reversible and irreversible phenomena. To model the energy balance of an electrochemical cell a Heat Transfer interface is used to model the heat transport whereas a current distribution interface (such as the Secondary Current Distribution) is used to generate the heat sources and sinks due to the electrochemical currents. The [Governing Equations](#) are discussed in this section.

## *Governing Equations*

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Heat sources are generated due to the following three irreversible voltage losses in an electrochemical cell:

- Charge transport in the electrolyte
- Charge transport in the solid conductor materials
- Activation overpotentials in the electrode reactions

In addition, reversible heat sources and sinks can appear due to the entropy changes in the electrode reactions.

### **JOULE HEATING DUE TO CHARGE TRANSPORT**

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

$$Q_{\text{JH}} = -(\mathbf{i}_s \cdot \nabla \phi_s + \mathbf{i}_l \cdot \nabla \phi_l)$$

For an electrode or electrolyte domain this is the total electrochemical heat source. For porous electrodes sources due to electrochemical reactions, it is added to the joule heating.

### **HEATING DUE TO ELECTROCHEMICAL REACTIONS**

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

$$\text{Heat generated} = \text{Total reaction enthalpy} - \text{Electrical energy leaving the system}$$



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

$$Q_m = \left( \frac{\Delta H_m}{n_m F} - \left( \frac{\Delta G_m}{n_m F} - \eta_{m, \text{tot}} \right) \right) i_m \quad (3-2)$$

where  $\Delta H_m$  is the enthalpy change of the reaction, and  $\Delta G_m$  is the *Gibbs free energy* of the reaction,  $\Delta G_m$ , defined as

$$\Delta G_m = \Delta H_m - T \Delta S_m$$

where  $\Delta S_m$  is the net entropy change. The equilibrium potential is related to  $\Delta G_m$  in the following way:

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

In Equation 3-2,  $\eta_{m, \text{tot}}$  is the total overpotential, which is defined as

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

By the relation

$$\frac{\partial E_{\text{eq}, m}}{\partial T} = \frac{\Delta S_m}{n_m F}$$

the local heat source due to the electrochemical conversion process becomes

$$Q_m = \left( \phi_s - \phi_l - E_{\text{eq}, m} + T \frac{\partial E_{\text{eq}, m}}{\partial T} \right) i_m$$

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,  $Q_{\text{EC}}$ , for an electrode surface is the sum of all individual heat sources of the electrode reactions according to

$$Q_{\text{EC}} = \sum_m Q_m$$



Add a **Boundary Heat Source** node to a Heat Transfer or Heat Transfer in Porous Media interface to couple to this heat source on a boundary.

---

For a porous electrode joule heating and electrochemical sources are summed up for a total heat source in the domain according to

$$Q_{\text{TOT},p} = \sum_m a_{v,m} Q_m + Q_{\text{JH}}$$



Add a **Heat Source** (described in the *COMSOL Multiphysics Reference Manual*) node to a Heat Transfer or Heat Transfer in Porous Media interface to couple to the total electrochemical heat source in a domain.

---

# 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*

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The Electrode, Shell interface solves for the electric potential  $\phi_s$  (SI unit: V) on a boundary, using the following governing equation:

$$\nabla_{\mathbf{T}} \cdot (s \mathbf{i}_s) = -i_n \quad (3-3)$$

where  $\nabla_{\mathbf{T}}$  is the tangential gradient operator,  $s$  (SI unit: m) is the electrode layer thickness, and  $i_n$  (SI unit: A/m<sup>2</sup>) 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<sup>2</sup>) is the tangential current density vector along the electrode boundary, defined as

$$\mathbf{i}_s = -\nabla_{\mathbf{T}} \sigma_s \phi_s \quad (3-4)$$

where  $\sigma_s$  is the electric conductivity (SI unit: S/m). The next section discusses [Coupling to Other Physics Interfaces](#).

## *Coupling to Other Physics Interfaces*

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### **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  $i_{\text{tot}}$  (SI unit:  $\text{A}/\text{m}^2$ ) 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

$$s = s_0 + \Delta s_{\text{tot}} \quad (3-5)$$

where  $s_0$  is the initial electrode layer thickness, and  $\Delta s_{\text{tot}}$  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:  $\text{W}/\text{m}^2$ ) according to

$$Q_H = -s \mathbf{i}_s \cdot \nabla_t \phi_s$$

# Theory for the Electroanalysis Interface

The [Electroanalysis Interface](#) theory is described in this section:

- [Electroanalytical Methods](#)
- [Supporting Electrolyte](#)
- [Domain Equations for the Electroanalysis Interface](#)
- [Electrodes in the Electroanalysis Interface](#)
- [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.

The Electroanalysis interface is designed for efficient simulation of electroanalytical methods. Many of the features found in the physics interface are shared with the

Current Distribution interfaces and Transport of Diluted Species interfaces, subject to the simplifying assumption of zero electric field in the electrolyte solution.



- [The Primary and Secondary Current Distribution Interfaces](#)
- [The Transport of Diluted Species Interface](#)

### *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 one of the Current Distribution interfaces should be used instead of the Electroanalysis interface.

### *Domain Equations for the Electroanalysis Interface*

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The Electroanalysis interface 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 interface 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  $i$ :

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

At zero electric field, this reduces to:

$$\mathbf{N}_i = -D_i \nabla c_i + c_i \mathbf{u} \quad (3-6)$$

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*:

$$\mathbf{N}_i = -D_i \nabla c_i$$

A mass balance also applies to each chemical species:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{N}_i = R_{i, \text{tot}} \quad (3-7)$$

The Electroanalysis interface solves [Equation 3-6](#) and [Equation 3-7](#) 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:

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i \quad (3-8)$$

Equation 3-8 is *Fick's second law of diffusion*.



The Electroanalysis interface 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 Tertiary Current Distribution, Nernst–Planck interface.



With the Electroanalysis interface, you can 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](#)

### *Electrodes in the Electroanalysis Interface*

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  $\phi_s$  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<sup>2</sup>) 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:

$$N_i = \sum_m \frac{\nu_{i,m} i_m}{n_m F} \quad (3-9)$$

where  $\nu_{i,m}$  is the stoichiometric coefficient of species  $i$  with respect to reaction  $m$  (in the reductive direction), and  $n_m$  is the number of electrons transferred.  $F$  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:

$$N_i = \mathbf{N}_i \cdot \mathbf{n} \quad (3-10)$$

[Equation 3-9](#) and [Equation 3-10](#) constitute the coupling between charge balance and mass balance in the Electroanalysis interface. This coupling only applies at the electrode–electrolyte interface, which is a boundary to the domain where the Electroanalysis 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](#):

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

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<sup>2</sup>) across the electrode area:

$$I_{\text{total}} = \int_{\partial\Omega} i_{\text{total}} ds$$



## Domain Equations for the Electroanalysis Interface

### *The Electroanalytical Butler–Volmer Equation*

A one-electron electrochemical reaction between two solution-phase species can be written as a reduction  $\text{Ox} + e^- \leftrightarrow \text{Red}$ .

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*:

$$i_{\text{loc}} = k_0 F \left( c_{\text{Red}} \exp\left(\frac{\alpha_a F \eta}{RT}\right) - c_{\text{Ox}} \exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right) \quad (3-11)$$

where  $k_0$  is the *heterogeneous rate constant* (SI unit: m/s) and  $\alpha_c$  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 3-11](#) into the Butler–Volmer equation written in terms of an exchange current density  $i_0$  (SI unit:  $\text{A}/\text{m}^2$ ):

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

The exchange current density  $i_0$  (SI unit:  $\text{A}/\text{m}^2$ ) is then related to the heterogeneous rate constant as  $i_0 = k_0 F c$ .

## *Counter Electrodes and Overall Charge Balance*

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The Electroanalysis interface 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:

$$\phi_{s, CE}: \int_{\text{electrodes}} i_{\text{tot}} dS = 0 \quad (3-12)$$

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

$$\eta_m = \phi_{s, CE} - E_{\text{eq}, m} \quad (3-13)$$

Note that only one counter electrode potential degree of freedom is added in the Electroanalysis interface, regardless of the number of counter electrodes that are active.



Domain Equations for the Electroanalysis Interface

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# Electrode Potentials and Reference Electrodes

In all the Electrochemistry branch interfaces, the dependent potential variables are  $\phi_s$  (SI unit: V), the electric potential of the electrode phase (the electron conductor, such as metal), and  $\phi_l$  (SI unit: V), the potential of the electrolyte phase (ion conductor).

Typically the kinetics of the electrochemical reactions are defined using the overpotential,  $\eta$  (SI unit: V), defined as

$$\eta = \phi_s - \phi_l - E_{\text{eq}} \quad (3-14)$$

where  $E_{\text{eq}}$  (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 3-14 is that it is the potential difference,  $\phi_s - \phi_l$ , that governs the kinetics, not the absolute individual values of  $\phi_s$  and  $\phi_l$ . 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:

$$\phi_{s, \text{ref}} = \phi_l + E_{\text{eq, ref}} \quad (3-15)$$

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:

$$E_{\text{vs ref}} = \phi_s - \phi_{s, \text{ref}} \quad (3-16)$$

Where  $E_{\text{vs ref}}$  (SI unit: V) is the electrode potential versus the defined the electric 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*

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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

$$\phi_{s, \text{bnd}} = E_{\text{vs ref}} + \phi_{s, \text{ref}} \quad (3-17)$$

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*

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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 3-15](#). 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 3-16, 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  $\phi_s$  (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 3-16, 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 3-17. 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 3-16, is also defined on these features.

# 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.



[Studies and Solvers](#) and [Building a COMSOL Multiphysics Model](#) in the *COMSOL Multiphysics Reference Manual*

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## *General Current Distribution Problems*

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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.
- 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 expected to deviate the least from equilibrium (usually the one with the fastest kinetics, for instance the hydrogen electrode in a PEM fuel cell) and assuming zero overpotentials for the main electrode reactions.
- Switch to **Linearized Butler-Volmer** kinetics 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 towards the electrolyte boundaries.



- 
- [Electrochemistry Interfaces](#)
  - [Specifying Initial Values](#) and [Meshing Techniques](#) in the *COMSOL Multiphysics Reference Manual*
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## *Electrochemistry Coupled to Mass Transport*

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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 cause issues in tertiary current distributions and battery simulations since that could imply that no charge carriers or no reacting material is present initially.
- If steep concentration gradients are expected close to electrode surfaces, use boundary layer meshing or finer size settings at these boundaries.
- When setting up user-defined kinetics expressions, avoid evaluating negative concentrations by using expressions such as  $\max(c, \text{eps}^2)$ , where  $\text{eps}$  is the machine epsilon, that is, a very small number.
- Try to solve for low currents / 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.



- [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*

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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 trouble-shooting a non-converging 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 using **Stationary with Initialization** or a **Time-dependent with Initialization** study 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 separately solve 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*:

- [Studies and Solvers](#)
- [Analyzing Model Convergence and Accuracy](#)
- [Achieving Convergence When Solving Nonlinear Equations](#)

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### *Time-dependent Problems with Load Steps*

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

- Use smoothed current/potential load functions in order to avoid discrete load steps.
- Add a double layer capacitance to the model, which can improve the numerical stability.
- Reduce the **Maximum step** taken by the solver if you want to prevent the solver from “missing” short square load steps, or change the **Steps taken by solver** setting from **Free** to **Strict**, or **Intermediate**, to control the time steps using the **Times** text field. Using the Events interface can also be an option in certain cases if the load cycle itself varies dynamically.



- [Double Layer Capacitance](#)

In the *COMSOL Multiphysics Reference Manual*:

- [Step and Time Dependent](#)
- [Building a COMSOL Multiphysics Model](#) and [The Events Interface](#)

## *Solver Settings*

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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.



In the *COMSOL Multiphysics Reference Manual*:

- [Studies and Solvers](#)
  - [Analyzing Model Convergence and Accuracy](#)
  - [Achieving Convergence When Solving Nonlinear Equations](#)
-



# Chemical Species Transport Interfaces

This chapter describes the physics interfaces found under the **Chemical Species Transport** 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 Transport of Diluted Species 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  $i$ .



Some features are only available in a limited set of add-on products. For a detailed overview of which features are available in each product, visit <http://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 `tds`.

## DOMAIN SELECTION

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

## TRANSPORT MECHANISMS

Diffusion is always included. By default, the **Convection** check box is selected under **Additional transport mechanisms**.

Note: Not all additional transport mechanisms listed below are available in all products. For detail see <http://www.comsol.com/products/specifications/>.


- Select the **Migration in electric field** check box to activate the migration transport of ionic species. See further the theory section [Adding Transport Through Migration](#).
- Select the **Adsorption in porous media** check box to activate the adsorption of solutes in porous media. See further [Adsorption](#).
- 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. See further [Theory for the Transport of Diluted Species Interface](#).

#### 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 options 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 checked, because this type of stabilization adds artificial diffusion and affects the accuracy of the original problem. However, this option can be used to get a good initial guess for under-resolved problems.

## ADVANCED SETTINGS

To display this section, click the **Show** button (  ) and select **Advanced Physics Options**. Normally these settings do not need to be changed. Select a **Convective term**—**Non-conservative 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 this section, click the **Show** button (  ) and select **Discretization**.

The **Compute boundary fluxes** check box is activated by default so that COMSOL 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, COMSOL 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) 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) is the normal total flux and corresponds to the boundary flux plus additional transport terms, for example, the convective flux when you use the non-conservative 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 **Concentration**  $c$  by default. The names must be unique with respect to all other dependent variables in the component.

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

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

## FURTHER READING



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	<ul style="list-style-type: none"><li>• <a href="#">Theory for the Transport of Diluted Species Interface</a></li><li>• <a href="#">Numerical Stabilization</a></li><li>• <a href="#">Domain, Boundary, and Pair Nodes for the Transport of Diluted Species Interface</a></li><li>• In the <i>COMSOL Multiphysics Reference Manual</i> see <a href="#">Table 2-3</a> for links to common sections and <a href="#">Table 2-4</a> to common feature nodes. You can also search for information: press F1 to open the <b>Help</b> window or Ctrl+F1 to open the <b>Documentation</b> window.</li></ul>
	<ul style="list-style-type: none"><li>• <i>Effective Diffusivity in Porous Materials</i>: Application Library path <b>COMSOL_Multiphysics/Diffusion/effective_diffusivity</b></li><li>• <i>Thin-Layer Diffusion</i>: Application Library path <b>COMSOL_Multiphysics/Diffusion/thin_layer_diffusion</b></li></ul>

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### *The Transport of Diluted Species in Porous Media Interface*

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This interface (  ), found under the **Chemical Species Transport** branch (  ), is used to calculate the species concentration and transport in free and porous media. It includes reaction rate expressions and solute sources for modeling of species transport and reaction in porous media. The interface is the same as the Transport of Diluted Species interface but it uses other defaults: A Porous Media Transport node is activated by default.

Note: Not all additional transport mechanisms listed below are available in all products. For details, see <http://www.comsol.com/products/specifications/>.

This interface includes free and porous media flow with immobile and mobile phases, including diffusion, convection, 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, provide an interface for defining the properties of the porous media, as well as additional properties governing adsorption, volatilization, dispersion and diffusion, 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

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	<ul style="list-style-type: none"><li>• <a href="#">Theory for the Transport of Diluted Species Interface</a></li><li>• <a href="#">Domain, Boundary, and Pair Nodes for the Transport of Diluted Species Interface</a></li></ul>
	<ul style="list-style-type: none"><li>• <i>Variably Saturated Flow and Transport—Sorbing Solute:</i> Application Library path <b>Subsurface_Flow_Module/Solute_Transport/sorbing_solute</b> Web link: <a href="http://http://www.comsol.com/model/variably-saturated-flow-and-transport-sorbing-solute-490">http://http://www.comsol.com/model/variably-saturated-flow-and-transport-sorbing-solute-490</a></li></ul>

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

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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 right-click 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.

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- Concentration
- Electrode-Electrolyte Interface Coupling
- Equilibrium Reaction
- Flux
- Flux Discontinuity
- Inflow
- Initial Values
- Line Mass Source<sup>1</sup>
- Mass-Based Concentrations
- No Flux
- Open Boundary
- Outflow
- Partially Saturated Porous Media
- Periodic Condition
- Point Mass Source
- Porous Electrode Coupling
- Porous Media Transport Properties
- Reaction Coefficients
- Reactions
- Species Source
- Surface Equilibrium Reaction
- Symmetry
- Thin Diffusion Barrier
- Thin Impermeable Barrier
- Transport Properties
- Volatilization

Some features may require certain add-on modules. See details <http://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 2-3](#) for links to common sections and [Table 2-4](#) 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.

### *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](#) sub-node is available from the context menu as well as from the **Physics** toolbar, **Attributes** menu. Note that this feature is only available in some COMSOL products. See details: <http://www.comsol.com/products/specifications/>.

#### **MODEL INPUTS**

If transport by convection is active, the velocity field of the solvent needs to be specified as a model input. Select the source of the **Velocity field  $\mathbf{u}$** . For **User defined**, enter values or expressions for the velocity components in the fields or table. This input option is always available.

You can also select the velocity field solved by a Fluid Flow interface that been added to the model component. These physics interfaces are available for selection from the **Velocity field** list if they are active in the domains. A list of the variable names related to the Fluid Flow interface will be visible in a table.

When the **Migration in electric field** check box is selected on the **Settings** window for **Transport of Diluted Species**, select the source of the electric potential field and, optionally, temperature.

- Enter values or expressions for the **Electric potential  $V$** , which is **User defined**; this input option is always available.
- Select the electromagnetic field solved by an AC/DC-based interface that has also been added to the model. This works like the velocity field model input described above.
- The default mobility model is the Nernst-Einstein relation. This also requires a temperature input, which will be exposed in the same manner as the electric potential described above.

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

## **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 **Anisotropic** 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 add-on products. See details: <http://www.comsol.com/products/specifications/>.



## **MIGRATION IN ELECTRIC FIELD**

This section is available when the **Migration in electric field** check box is selected. 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 **Anisotropic**—and type in the value of expression of the mobility  $u_{m,e}$ .

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

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

#### EXAMPLE MODELS

	<p><i>Separation Through Dialysis</i>: Application Library path <b>Chemical_Reaction_Engineering_Module/Separation_Processes/dialysis</b></p> <p>Web link: <a href="http://www.comsol.com/model/separation-through-dialysis-258">http://www.comsol.com/model/separation-through-dialysis-258</a></p>
	<p><i>Transport in an Electrokinetic Valve</i>: Application Library path <b>Microfluidics_Module/Fluid_Flow/electrokinetic_valve</b></p> <p>Web link: <a href="http://www.comsol.com/model/electrokinetic-valve-603">http://www.comsol.com/model/electrokinetic-valve-603</a></p>

#### *Turbulent Mixing*

Note that the Turbulent Mixing node is only available for some product add-ons. See details: <http://www.comsol.com/products/specifications/>.

This subnode is available from the context menu (right-click the **Transport Properties** parent node) as well as from the **Physics** toolbar, **Attributes** menu, if **Convection** is selected as a transport mechanism. Use this node to account for the turbulent mixing caused by the eddy diffusivity. An example is when the specified velocity field corresponds to a RANS solution.

#### TURBULENT MIXING PARAMETERS

Some physics interfaces provide the turbulent kinematic viscosity, and these appear as options in the **Turbulent kinematic viscosity**  $\nu_T$  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](#) (this link is available if you have the CFD Module documentation installed)



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*Turbulent Mixing of a Trace Species*: Application Library path  
**CFD\_Module/Single-Phase\_Tutorials/turbulent\_mixing**

Web link:

[http://www.comsol.com/model/  
turbulent-mixing-of-a-trace-species-12727](http://www.comsol.com/model/turbulent-mixing-of-a-trace-species-12727)

---

## *Initial Values*

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

### DOMAIN SELECTION

If there are several types of domains with different initial values defined, it might be necessary to remove some domains from the selection. These are then defined in an additional **Initial Values** node.

### INITIAL VALUES

Enter a value or expression for the initial value of the **Concentration** or concentrations,  $c_i$ . This also serves as a start guess for stationary problems.

## *Mass-Based Concentrations*

Use the **Mass-Based Concentrations** node to add postprocessing variables for mass-based concentrations (SI unit:  $\text{kg}/\text{m}^3$ ) and mass fractions (dimensionless) for all the species.

### MIXTURE PROPERTIES

The default **Solvent density**  $\rho_{\text{solvent}}$  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:  $\text{mol}/(\text{m}^3 \cdot \text{s})$ ), 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. See example in the application *Fine Chemical Production in a Plate Reactor* as linked below.

### REACTING VOLUME

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 non-porous domains, the settings of the Reacting Volume section has no impact.

Note that the Reacting Volume section is only available in the products that provide the Transport of Diluted Species in Porous Media interface. See details: <http://www.comsol.com/products/specifications/>.

For **Total volume** the reaction expressions in  $\text{mol}/(\text{m}^3 \cdot \text{s})$  are specified per unit volume of the model domain (multiplied by unity).

For **Pore volume** the reaction expressions in  $\text{mol}/(\text{m}^3 \cdot \text{s})$  are specified per unit volume of total pore space. The reaction expressions will be multiplied by the domain porosity,  $\epsilon_p$ . ( $\epsilon_p$  equals unity for non-porous domains).

For **Liquid phase** the reaction expressions in  $\text{mol}/(\text{m}^3 \cdot \text{s})$  are specified per unit volume of liquid in the pore space. The expressions will be multiplied by the liquid volume fraction  $\theta$ . ( $\theta$  equals  $\epsilon_p$  for Saturated Porous Media domains).

For **Gas phase** the expressions are multiplied by the gas volume fraction  $\alpha_v = \varepsilon_p - \theta$ .  $\alpha_v$  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: <http://www.comsol.com/model/fine-chemical-production-in-a-plate-reactor-8589>

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#### *No Flux*

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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.

#### *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<sup>3</sup>) 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: <http://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 point-wise 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**. See the details about the different constraint setting in the section [Constraint Reaction Terms](#) in the *COMSOL Application*.

### FURTHER READING

See the theory chapter in the section [Danckwerts Inflow Boundary Condition](#).

### *Outflow*

---

This node is not available if **Diffusion** only is included in the model.

Set this condition at outlets where species are transported out of the model domain by fluid motion. It is assumed that convection is the dominating transport mechanism across outflow boundaries, and therefore that diffusive transport can be ignored, that is:

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

### *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 (SI unit: mol/m<sup>3</sup>) 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**. See the details about the different constraint setting in the section [Constraint Reaction Terms](#) in the *COMSOL Multiphysics Reference Manual*.

### *Flux*

---

This node can be used to specify the total species flux across a boundary. The total flux of species  $c$  is defined accordingly:

where  $N_0$  is an arbitrary user-specified flux expression (SI unit: mol/(m<sup>2</sup>·s)). For example,  $N_0$  can represent a flux from or into a much larger surrounding environment, a phase change, or a flux due to chemical reactions.  $N_0$  can also be a function of the concentration and the electric potential (if the mass transport includes migration of ionic species).

When diffusion is the only transport mechanism present, the flux condition is extended to include a mass transfer term to describe flux into a surrounding environment:

$$-\mathbf{n} \cdot (-D\nabla c) = N_0 + k_c(c_b - c)$$

where  $k_c$  is a mass transfer coefficient (SI unit: m/s), and  $c_b$  is the concentration (SI unit: mol/m<sup>3</sup>) in the surroundings of the modeled system (the bulk concentration). The mass transfer coefficient (to be specified) is often given by boundary-layer theory.

### **INWARD FLUX**

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

Note: Use a minus sign when specifying a flux leaving the system.

### *Symmetry*

---

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

This boundary condition is identical to that of the [No Flux](#) node, but applies to all species and cannot be applied to individual species.

## Flux Discontinuity

---

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

$$-\mathbf{n} \cdot (\mathbf{N}_d - \mathbf{N}_u) = N_0 \quad \mathbf{N} = (c\mathbf{u} - D\nabla c - zu_m Fc\nabla\phi)$$

where the value  $N_0$  (SI unit: mol/(m<sup>2</sup>·s)) specifies the jump in 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.

## Periodic Condition

---

The **Periodic Condition** node can be used to define periodicity or antiperiodicity between two boundaries. The node can be activated on more than two boundaries, in which case the feature tries to identify two separate surfaces that can each consist of 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.

For information about the **Orientation of Source** section, see [Orientation of Source and Destination](#) in the *COMSOL Multiphysics Reference Manual*.

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 the application example:



- *The KdV Equation and Solitons*: Application Library path **COMSOL\_Multiphysics/Equation\_Based/kdv\_equation**
-

## *Line Mass Source*

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

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

For the “Reacting Flow in Porous Media, Diluted Species” interface, which is available in some add-on products, the **Line Mass Source** node is available in two versions, 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 symmetry axis and the symmetry axis
3D	Edges

### **SPECIES SOURCE**

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

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

### **FURTHER READING**

See the section [Mass Sources for Species Transport](#) in the *COMSOL Multiphysics Reference Manual*.

## *Point Mass Source*

---

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

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

For the “Reacting Flow in Porous Media, Diluted Species” interface, which is available in some add-on products, the **Point Mass Source** node is available in two versions, one for the fluid flow (**Fluid Point Source**) and one for the species (**Species Point Source**).

### **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](#) in the *COMSOL Multiphysics Reference Manual*.

### *Open Boundary*

---

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

Use this node to set up mass transport across boundaries where both convective inflow and outflow can occur. Use this boundary condition to specify an exterior species concentration on parts of the boundary where fluid flows into the domain. A condition equivalent to the **Outflow** node applies to the parts of the boundary where fluid flows out of the domain.

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

### **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. To set up the node, specify the layer thickness and a diffusion coefficient for each transported species.

### THIN DIFFUSION BARRIER

Enter a **Layer thickness**  $d_s$  (SI unit: m). The default is 0.005 m (5 mm). Enter a **Diffusion coefficient**  $D_{s,c}$  (SI unit:  $m^2/s$ ). The default is 0.

#### *Thin Impermeable Barrier*

---

This feature models a thin mass transfer barrier. The feature is available on interior boundaries and introduces a discontinuity in the concentration across the boundary. On each side of the boundary a no flux condition is prescribed for the mass transport. The Thin Impermeable Barrier boundary 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 or Rotating Interior Wall feature in order to model a thin solid wall.

#### *Equilibrium Reaction*

---

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

Use this node to model an equilibrium reaction in a domain. This feature is available with two species or more.

The equilibrium reaction is defined by the relation between the chemical activities of the chemical species participating in the reaction (the equilibrium condition), and the stoichiometry of the reaction.

The node solves for an additional degree of freedom (the reaction rate) 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.

### 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). The default is 1. Enter a value or expression for the **Unit activity concentration**  $C_{a0}$  (SI unit:  $mol/m^3$ ). The default is  $1 \times 10^{-3} mol/m^3$ . **Equilibrium constant** creates an equilibrium

condition based on the stoichiometric coefficients, the species activities, and the law of mass action.

For **User defined** enter an **Equilibrium expression**  $E_{\text{eq}}$  (dimensionless).

#### STOICHIOMETRIC COEFFICIENTS

Enter a value for the stoichiometric coefficient  $\nu_c$  (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 Equilibrium Reaction*

---

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

Use this node to model an equilibrium reaction on a boundary (surface). The settings for this node are similar to [Equilibrium Reaction](#).

#### *Porous Electrode Coupling*

---

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

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 modeling also the momentum transport and expect a non-negligible 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.

### *Reaction Coefficients*

---

Add this node to the [Electrode-Electrolyte Interface 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.

All current densities from the [Electrode Reaction](#) ( $i_{1oc}$ , SI unit: A/m<sup>2</sup>) or the [Porous Electrode Reaction](#) ( $i_v$ , SI unit: A/m<sup>3</sup>) nodes 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 [Electrode Reaction](#) documentation or the theory section.

Use multiple subnodes to couple to multiple reactions.

---

## Theory for the Coupling of Mass Transport to Electrochemical Reactions

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### *Electrode-Electrolyte Interface Coupling*

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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.

In the Transport of Concentrated Species interface the molar fluxes are multiplied by the species molar masses to obtain the corresponding mass fluxes.

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

## Porous Media Transport Properties

---

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

Use this node to model the transport of diluted species in porous media.

### MATRIX PROPERTIES

Select an option from the **Porous material** list. The default is **Domain material**.

By default the **Porosity**,  $\varepsilon_p$  (dimensionless) is taken **From material**. For **User defined** enter a different value. The default is 0.3.

When the **Adsorption in porous media** check box is selected on the **Settings** window for the physics interface, the default **Density**  $\rho$  (SI unit: kg/m<sup>3</sup>) is taken **From material**. For **User defined** enter a different value. The default is 1400 kg/m<sup>3</sup>.

### DIFFUSION

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

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

### ADSORPTION

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

Select a **Sorption type**—**Langmuir** (the default), **Freundlich**, or **User defined**.

- For **Langmuir** enter a **Langmuir constant**  $k_{L,c}$  (SI unit: m<sup>3</sup>/mol) and an **Adsorption maximum**  $c_{p,max,c}$  (SI unit: mol/kg). The defaults are 0 m<sup>3</sup>/mol and 0 mol/kg, respectively.
- For **Freundlich** enter a **Freundlich constant**  $k_{F,c}$  (dimensionless), a **Freundlich exponent**  $N_{F,c}$  (dimensionless), and **Reference concentration**  $c_{ref,c}$  (SI unit: m<sup>3</sup>/mol).
- For **User defined** enter an **Adsorption isotherm**  $k_{P,c}$  (SI unit: m<sup>3</sup>/kg).



## 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:  $\text{m}^2/\text{s}$ ) 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 **Anisotropic** based on the properties of the dispersion tensor.

Select **Dispersivity** when **Convection** has been added as transport mechanism. Specify the dispersivities (SI unit: m) to define the dispersion tensor  $D_D$  (SI unit:  $\text{m}^2/\text{s}$ ) together with the velocity field  $\mathbf{u}$ . 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.

## FURTHER READING

See the theory chapter in the section [Transport of Diluted Species in Porous Media](#).

### *Partially Saturated Porous Media*

---

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

Use this node to model the transport of diluted species in partially saturated porous media.

## 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  $\theta$  (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).

## **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.

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**.

## **ADSORPTION**

This section is available when the **Adsorption 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](#).

## **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 only available in a limited set of add-on products. See <http://www.comsol.com/products/specifications/> for more details on availability.

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 the boundary condition to model a thin layer through which mass is transported by volatilization only. To set up the node, specify the layer thickness and the atmospheric concentration of each species in the thin layer for each transported species.

#### **VOLATILIZATION**

Enter a **Layer thickness**  $d_s$  and the atmospheric concentration for each species. The **Gas diffusion coefficient**  $D_{G,c}$  (SI unit:  $\text{m}^2/\text{s}$ ) and the **Volatilization** coefficient  $k_{G,c}$  (dimensionless) for each species are taken from the adjacent **Partially Saturated Porous Media** domain.

#### *Reactive Pellet Bed*

---

Note that this feature is only available if you are licensed to the Chemical Reaction Engineering Module. See details: <http://www.comsol.com/products/specifications>.

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 Initial values are added.

#### **BED PARAMETERS**

Here you can specify the bed porosity which is the void fraction between the pellets in the packed bed structure. Either you can specify the densities of the bed and one pellet, **Density** option, or specify the porosity directly **Porosity** option.

#### **PELLET SIZE DISTRIBUTION**

Different pellet sizes can be modeled in the same bed. 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. Then based on this choice enter the following as applicable:

- **Radius**  $r_{pe}$  (SI unit: m). The default is  $1 \times 10^{-3}$  m.
- **Radii and volume percentages**: If several sizes are selected, the radius of each size, and its volume percentage of the total pellet volume must be added.

Note that different chemical reactions can be specified for each size of the pellet.

#### **PELLET PARAMETERS**

Enter a **Pellet porosity**  $\varepsilon_{pe}$  (dimensionless) to account for a porous pellet.

Select **Diffusion model**—**Millington and Quirk model** (the default), **Bruggeman model**, **Tortuosity model**, or **User defined** to describe the correction of the diffusion coefficient in the pellet. In the case of the **Tortuosity model** a value for the tortuosity  $\tau_{pe}$  within the pellet needs to be set.

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

#### PELLET-FLUID SURFACE

The pellet surface to fluid coupling has two **Coupling type** options available:

- **Continuous concentration**,  $c_{pei}=c_i$ , assuming no resistance to the mass transport between pellet and fluid. This option assumes that all the resistance against mass transfer is inside the pellet pores.
- **Film resistance (mass flux)** when the above assumption does not hold and the mass transfer is also limited by the convective and diffusional properties of the fluid surrounding the pellet. This option employs a film resistance theory as described in the section [Theory for the Reactive Pellet Bed](#).

The **Film resistance (mass flux)** option computes the inward surface flux,  $N_{i,inward}=h_{Di}(c_i-c_{pei})$ .  $h_{Di}$  is the mass transfer coefficient (SI unit:  $m/s$ ) and can be 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 in most cases apply for spherical dumped pellets or otherwise use the **User defined** option.

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 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 setting 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: <http://www.comsol.com/model/a-multiscale-3d-packed-bed-reactor-17019>

## *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<sup>3</sup>·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 strain can be written as

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

where  $\beta_h$  is the coefficient of hygroscopic swelling,  $c_{mo}$  is the moisture concentration, and  $c_{mo,ref}$  is the strain-free reference concentration.



It 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 <http://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 Node](#) in the *COMSOL Multiphysics Reference Manual*.



# The Nernst-Planck-Poisson Equations Interface

The **Nernst-Planck-Poisson Equations** interface ()<sup>a</sup>, 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](#) ()<sup>a</sup>. (with Migration enabled), that solves for the Nernst-Planck equations without charge neutrality, and [The Electrostatics Interface](#) ()<sup>a</sup>, that solves for the Poisson's equation.



A [Space Charge Density Coupling](#) ()<sup>a</sup> 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.

	<ul style="list-style-type: none"><li>• <a href="#">The Multiphysics Node</a> in the <i>COMSOL Multiphysics Reference Manual</i>.</li><li>• <a href="#">The Transport of Diluted Species Interface</a>.</li><li>• <a href="#">The Electrostatics Interface</a></li><li>• <a href="#">Space Charge Density Coupling</a></li><li>• <a href="#">Potential Coupling</a></li></ul>
	<ul style="list-style-type: none"><li>• <a href="#">Diffuse Double Layer</a> tutorial in the application library.</li></ul>



# 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.



**Zone Electrophoresis:** Application Library path **Electrochemistry\_Module/Electrochemical\_Engineering/zone\_electrophoresis**

---

## SETTINGS

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

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

The default **Name** (for the first physics interface in the model) is `e1`.

### DOMAIN SELECTION

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

### OUT-OF-PLANE THICKNESS



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

### CROSS SECTIONAL AREA



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

### 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 Porosity node is can be added to a domain to specify the electrolyte volume fraction, and the Effective Transport Parameter Correction sections are enabled in the species nodes.

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

## ADVANCED SETTINGS

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

## CONCENTRATION DISCRETIZATION AND DISCRETIZATION SECTIONS

To display these sections, click the **Show** button (  ) and select **Discretization**.

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

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

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 `phi` 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



- [Numerical Stabilization](#) in the *COMSOL Multiphysics Reference Manual*.
- In the *COMSOL Multiphysics Reference Manual*, see [Table 2-3](#) for links to common sections and [Table 2-4](#) 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 its  $pK_a$  (the acid equilibrium constant) parameter, and each dissociation step adds one additional subspecies concentration variable. For dissociation species 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 nodes 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  $\langle \text{name} \rangle . c_{\langle \text{species\_name} \rangle}$  where  $\langle \text{name} \rangle$  is the name of the interface (default is e1), set on the interface top node, and  $\langle \text{species\_name} \rangle$  is the **Species name**. For dissociation species nodes defining multiple subspecies, the concentration nodes are named as  $\langle \text{name} \rangle . c_{\langle X \rangle}_{\langle \text{species\_name} \rangle}$  where  $\langle X \rangle$  is the integer from 1 up to the total number of subspecies. Note that the **Solvent** node automatically defines the concentration variables for protons ( $\langle \text{name} \rangle . c_H$ ) and hydroxide ions ( $\langle \text{name} \rangle . c_{OH}$ ).

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 checkbox 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** edit field. The contribution to the electrolyte current for immobile species is zero.

### *Diffusion and Migration Settings*

---

All species, except when the **Immobile Species** checkbox 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  $\text{m}^2/\text{s}$ ) or the **Mobility** (SI-unit:  $\text{s}\cdot\text{mol}/\text{kg}$ ). 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  $\text{m}^2/(\text{V}\cdot\text{s})$ , whereas COMSOL uses  $\text{s}\cdot\text{mol}/\text{kg}$ . To convert mobilities expressed in  $\text{m}^2/(\text{V}\cdot\text{s})$  to the corresponding values in  $\text{s}\cdot\text{mol}/\text{kg}$ , you typically divide by the Faraday constant,  $F_{\text{const}}$  (96485 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 [Porosity](#) node.

## IONIC STRENGTH CONTRIBUTION

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

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
- Porosity
- 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 2-3](#) for links to common sections and [Table 2-4](#) 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 may 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 ( $\langle \text{name} \rangle . \text{cH}$ ) and hydroxide ions ( $\langle \text{name} \rangle . \text{cOH}$ ), 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.

### *Porosity*

---

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) 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.

See also [Common Settings for the Species nodes in the Electrophoretic Transport Interface](#) and [Diffusion and Migration Settings](#).

### *Ampholyte*

---

Use the **Ampholyte** node generically to define any species where the average charge depends on the pH of the solution. The **Dissociation model** may be based either on a set of **Equilibrium constants** or an **Average charge**.

When using the **Equilibrium constants** the **Base charge in last dissociation step**,  $Z_0$  (unitless), needs to be set.

The **Average charge**,  $\bar{Z}$  (unitless) parameter is typically a function of pH and may be added as an analytical function or an interpolation polynomial under **Definitions**. The average squared charge, used in the electrolyte potential equation, is calculated automatically based on  $\bar{Z}$ .

See also [Common Settings for the Species nodes in the Electrophoretic Transport Interface](#) and [Diffusion and Migration Settings](#).

### *Protein*


---

Use the **Protein** node to define macromolecules. The features of the Protein node are similar to the [Ampholyte](#) node, but with the default settings applicable for larger molecules.

See also [Common Settings for the Species nodes in the Electrophoretic Transport Interface](#) and [Diffusion and Migration Settings](#).

### *Current Source*

---

To make this node available, click the **Show** button (  ) and select **Advanced Physics Options**.

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, that 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,  $\phi_l$ , to be equal to the **Boundary electrolyte potential**,  $\phi_{l, \text{bnd}}$  (SI unit: V).

#### **CONSTRAINT SETTINGS**

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

### *Species Source*

---

To make this node available, click the **Show** button () and select **Advanced Physics Options**.

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:  $\text{mol}/(\text{m}^3 \cdot \text{s})$ ) 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**,  $c$  ( $\text{mol}/\text{m}^3$ ), 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 total 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.

Note: Use a minus sign when specifying a flux leaving the system.

### *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<sup>2</sup>) and the bulk concentrations,  $c_{b,i}$  (SI unit: mol/m<sup>2</sup>).

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**  $cb_1$ ,  $cb_2$ ,  $cb_3$ ...are then listed in the table.

### DISCRETIZATION

To display this section, click the **Show** button (  ) and select **Discretization**.

### CONSISTENT AND INCONSISTENT STABILIZATION

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

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*

---

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 2-3](#) for links to common sections and [Table 2-4](#) 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**  $\Gamma_s$  (SI unit: mol/m<sup>2</sup>). The default is  $2 \times 10^{-5}$  mol/m<sup>2</sup>.

Enter a **Site occupancy number**  $\sigma_i$  (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<sup>2</sup>/s) is **User defined**. Select **Isotropic**, **Diagonal**, **Symmetric**, or **Anisotropic** 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**  $\rho_i$  (SI unit: kg/m<sup>3</sup>). The default molar mass is 0.144 kg/mol and the default density is 5320 kg/m<sup>3</sup>.

This section is only present if the number of bulk species is 1 or higher.



## Surface Reaction Equations on Deforming Geometries

---

### *Initial Values*

---

The **Initial Values** node allows the initial value or guess for the surface and bulk concentrations.

#### INITIAL VALUES

Based on the number of surface species and number of bulk species entered for the physics interface under Dependent Variables section, enter values for the same number of **Surface concentration**  $cs, cs2, cs3...$  (SI unit: mol/m<sup>2</sup>) and **Bulk concentration**  $cb, cb2, cb3...$  (SI unit: mol/m<sup>2</sup>) 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<sup>2</sup>·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<sup>2</sup>·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,  $c_{s,0,cs1,cs2\dots}$  (SI unit: mol/(m<sup>2</sup>·s)).

### **CONSTRAINT SETTINGS**

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

# 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 of 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:

- [Mass Balance Equation](#)
- [Equilibrium Reaction Theory](#)
- [Convective Term Formulation](#)
- [Solving a Diffusion Equation Only](#)
- [Mass Sources for Species Transport](#)
- [Crosswind Diffusion](#)
- [Adding Transport Through Migration](#)
- [Theory for the Reactive Pellet Bed](#)
- [Supporting Electrolytes](#)
- [Danckwerts Inflow Boundary Condition](#)
- [References](#)

The [Transport of Diluted Species in Porous Media Interface](#) theory is also included.

## 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  $i$ :

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D\nabla c_i) + \mathbf{u} \cdot \nabla c_i = R_i \quad (4-1)$$

Equation 4-1 in its form above includes the transport mechanisms diffusion and convection. If *Migration in Electric Field* is activated (only available in some add-on products), the migration mechanism will be added to the equation as well. See more details in the section [Adding Transport Through Migration](#).

- $c_i$  is the concentration of the species (SI unit: mol/m<sup>3</sup>)
- $D_i$  denotes the diffusion coefficient (SI unit: m<sup>2</sup>/s)
- $R_i$  is a reaction rate expression for the species (SI unit: mol/(m<sup>3</sup>·s))
- $\mathbf{u}$  is the velocity vector (SI unit: m/s)

The flux vector  $\mathbf{N}$  (SI unit: mol/(m<sup>2</sup>·s)) is associated with the mass balance equation above and used in boundary conditions and flux computations. For the case where the diffusion and convection are the only transport mechanisms, the flux vector is defined as

$$\mathbf{N}_i = -D\nabla c + \mathbf{u}c \quad (4-2)$$

If *Migration in Electric Fields* is activated, the flux vector is amended with the migration term as show in the section [Adding Transport Through Migration](#).

The first term on the left-hand side of Equation 4-1 corresponds to the accumulation (or indeed consumption) of the species.

The second term accounts for the diffusive transport, accounting for the interaction between the dilute species and the solvent. A user input field for the diffusion coefficient is available. Anisotropic diffusion coefficient tensor input is supported.

The third term on the left hand side of Equation 4-1 describes the convective transport due to a velocity field  $\mathbf{u}$ . This field can be expressed analytically or be obtained from coupling this physics interface to one that computes fluid flow, such as *Laminar Flow*.

On the right-hand side of the mass balance equation (Equation 4-1),  $R_i$  represents a source or sink term, typically due to a chemical reaction, or /desorption on a porous matrix. To specify  $R_i$ , another node must be added to the Transport of Diluted Species

interface—the **Reaction** node, which has a field for specifying a reaction equation 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,  $\nu_i$  (dimensionless), of the reaction, the species activities of the reacting species  $a_i$  (dimensionless), and an equilibrium constant,  $K_{\text{eq}}$  (1) according to:

$$K_{\text{eq}} = \frac{\prod_{i \in \text{products}} a_i^{\nu_i}}{\prod_{i \in \text{reactants}} a_i^{-\nu_i}}$$

where the species activities are defined as

$$a_i = \gamma_{e,i} \frac{c_i}{c_{a0}}$$

where  $c_{a0}$  (SI unit: mol/m<sup>3</sup>) is the standard molarity, and  $\gamma_{e,i}$  (dimensionless) an activity coefficient.

Defining the stoichiometric coefficients positive for products and negative for reactants, the above equilibrium condition can also be written:

$$K_{\text{eq}} = \prod_i a_i^{\nu_i}$$

The [Equilibrium Reaction](#) node solves for a reaction rate so that the equilibrium condition is always fulfilled in the domain.



$\gamma_{e,i}$  is set to unity when the Equilibrium constant is selected on the Settings window. For non-unity 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 non-equilibrium 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 (a check box to activate migration is available) and implements the mass balance equation in [Equation 4-1](#).

There are two ways to present a mass balance where chemical species transport occurs through diffusion and convection. These are the non-conservative and conservative formulations of the convective term:

$$\text{non-conservative: } \frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c = \nabla \cdot (D\nabla c) + R \quad (4-3)$$

$$\text{conservative: } \frac{\partial c}{\partial t} + \nabla \cdot (c\mathbf{u}) = \nabla \cdot (D\nabla c) + R \quad (4-4)$$

and each is treated slightly differently by the solver algorithms. In these equations  $D$  (SI unit:  $\text{m}^2/\text{s}$ ) is the diffusion coefficient,  $R$  (SI unit:  $\text{mol}/(\text{m}^3 \cdot \text{s})$ ) is a production or consumption rate expression, and  $\mathbf{u}$  (SI unit:  $\text{m}/\text{s}$ ) 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 non-conservative formulation above. This is in fact the default formulation in this physics interface and ensures that nonphysical source terms do not emerge from a solution for the flow field. 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 4-3](#) and [Equation 4-4](#) by clearing the Convection check box in the Transport Mechanisms section for [The Transport of Diluted Species Interface](#). The equation then becomes

$$\frac{\partial c}{\partial t} = \nabla \cdot (D\nabla c) + R$$

There are two types of mass sources in the Transport of Diluted Species interface: point sources and line sources.

---

**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 <http://www.comsol.com/products/specifications/>

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### POINT SOURCE

A point source is theoretically formed by assuming a mass injection/ejection,  $\dot{Q}_c$  (SI unit: mol/(m<sup>3</sup>·s)), in a small volume  $\delta V$  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

$$\lim_{\delta V \rightarrow 0} \int_{\delta V} \dot{Q}_c = \dot{q}_{p,c} \quad (4-5)$$

An alternative way to form a point source is to assume that mass is injected/extracted through the surface of a small object. Letting the object surface area tend to zero while keeping the mass flux constant, results in the same point source. For this alternative approach, effects resulting from the physical object's volume need to be neglected.

The weak contribution

$$\dot{q}_{p,c} \text{test}(c)$$

is added at a point in the geometry. As can be seen from Equation 4-5,  $\dot{Q}_c$  must tend to plus or minus infinity as  $\delta V$  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 4-5 corresponds to a finite concentration at a point with the effect of the point source spread out over a region around the point. The size of the region depends on the mesh and on the strength of



the source. A finer mesh gives a smaller affected region, but also a more extreme concentration value. It is important not to mesh too finely around a point source since this can result in unphysical concentration values. It can also have a negative effect on the condition number for the equation system.

### LINE SOURCE

A line source can theoretically be formed by assuming a source of strength  $\dot{Q}_{l,c}$  (SI unit: mol/(m<sup>3</sup>·s)), located within a tube with cross-section  $\delta S$  and then letting  $\delta S$  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

$$\lim_{\delta S \rightarrow 0} \int_{\delta S} \dot{Q}_{l,c} = \dot{q}_{l,c} \quad (4-6)$$

As in the point source case, an alternative approach is to assume that mass is injected/extracted through the surface of a small object. This results in the same mass source, but requires that effects resulting from the physical object's volume are neglected.

The weak contribution

$$\dot{q}_{l,c} \text{test}(e)$$

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](#) in the *COMSOL Multiphysics Reference Manual*.

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### *Adding Transport Through Migration*

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**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 <http://www.comsol.com/products/specifications/>

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In addition to transport due to convection and diffusion, the Transport of Diluted Species interface supports ionic species transport by *migration*. This is done by selecting the Migration in Electric Field check box under the Transport Mechanisms section for the physics interface. The mass balance then becomes:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i - z_i u_{m,i} F c_i \nabla V + c_i \mathbf{u}) = R_i \quad (4-7)$$

where

- $c_i$  (SI unit: mol/m<sup>3</sup>) denotes the concentration of species  $i$
- $D_i$  (SI unit: m<sup>2</sup>/s) is the diffusion coefficient of species  $i$
- $\mathbf{u}$  (SI unit: m/s) is the fluid velocity
- $F$  (SI unit: A·s/mol) refers to Faraday's constant
- $V$  (SI unit: V) denotes the electric potential
- $z_i$  (dimensionless) is the charge number of the ionic species, and
- $u_{m,i}$  (SI unit: mol·s/kg) its ionic mobility

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 ElectrostaticsSecondary Current Distribution interface. Sometimes it is assumed to be a supporting electrolyte, which simplifies the transport equations.

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) the temperature.

---

**Note:** With regards to migration, the assumption in the Transport of Diluted Species Interface is that the concentrations are so low that each ionic species does not contribute to a net charge in the solution. If this assumption does not hold, the physics interface called *Nernst-Planck Equations* needs to be used. This latter 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.

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### *Supporting Electrolytes*

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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:

$$\mathbf{i} = F \sum_j -z_j^2 u_{m,j} F c_j \nabla \phi \quad (4-8)$$

Equation 4-8 is simply Ohm's law for ionic current transport and can be simplified to

$$\mathbf{i} = -\kappa \nabla \phi \quad (4-9)$$

where  $\kappa$  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 4-9](#) yields:

$$\nabla \cdot (-\kappa \nabla \phi) = 0 \quad (4-10)$$

[Equation 4-10](#) can be easily solved using the Electrostatics or Secondary Current Distribution interface and, when coupled to the Transport in Diluted Species interface, the potential distribution shows up in the migration term.

### *Crosswind Diffusion*

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Transport of diluted species applications can often result in models with very high cell Péclet number—that is, systems where convection or migration dominates over diffusion. Streamline diffusion and crosswind diffusion are of paramount importance to obtain physically reasonable results. The Transport of Diluted Species interface provides two crosswind diffusion options using different formulations. Observe that crosswind diffusion makes the equation system nonlinear even if the transport equation is linear.

#### **DO CARMO AND GALEÃO**

This is the formulation described in [Numerical Stabilization](#). The method reduces over- and undershoots to a minimum, even for anisotropic meshes.

In some cases, the resulting nonlinear equation system can be difficult to converge. This can happen when the cell Péclet number is very high and the model contains many thin layers such as contact discontinuities. You then have three options:

- Refine the mesh, especially in regions with thin layers.
- Use a nonlinear solver with a constant damping factor less than one.
- Switch to the Codina crosswind formulation.

#### **CODINA**

The Codina formulation is described in [Ref. 1](#). It adds diffusion strictly in the direction orthogonal to the streamline direction. Compared to the do Carmo and Galeão formulation, the Codina formulation adds less diffusion but is not as efficient at reducing over- and undershoots. It also does not work as well for anisotropic meshes.

The advantage is that the resulting nonlinear system is easier to converge and that under-resolved 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 inlet concentrations and the fluid velocity. In chemical engineering this type of flux boundary condition is also known as a Danckwerts condition.

Use the Danckwerts condition to specify inlet concentrations to domains where high reaction rates are anticipated in the vicinity to the inlet ([Ref. 2](#)).

Given an inlet concentration  $c_{i,0}$  the Danckwerts inflow boundary condition reads

$$\mathbf{n} \cdot \mathbf{N}_i = \mathbf{n} \cdot (\mathbf{u} c_{i,0})$$

See further:



Inflow

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### *Transport of Diluted Species in Porous Media*

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#### **VARIABLY SATURATED POROUS MEDIA**

The following equations for the 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:

$$\begin{aligned} \frac{\partial}{\partial t}(\theta c_i) + \frac{\partial}{\partial t}(\rho_b c_{P,i}) + \frac{\partial}{\partial t}(\alpha_v c_{G,i}) + \mathbf{u} \cdot \nabla c_i = \\ \nabla \cdot [(D_{D,i} + D_{e,i}) \nabla c_i] + R_i + S_i \end{aligned} \quad (4-11)$$

On the left-hand side of [Equation 4-11](#), 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 4-11  $c_i$  denotes the concentration of species  $i$  in the liquid (SI unit: mol/m<sup>3</sup>),  $c_{P,i}$  the amount adsorbed to (or desorbed from) 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  $\epsilon_p$ , the liquid volume fraction  $\theta$ ; the bulk (or drained) density,  $\rho_b = (1 - \epsilon_p)\rho$ , and the solid phase density  $\rho$  (SI unit: kg/m<sup>3</sup>).

For saturated porous media, the liquid volume fraction  $\theta$  is equal to the porosity  $\epsilon_p$ , but for partially saturated porous media, they are related by the saturation  $s$  as  $\theta = s\epsilon_p$ . The resulting gas volume fraction is  $\alpha_v = \epsilon_p - \theta = (1-s)\epsilon_p$ .

On the right-hand side of Equation 4-11, the first term introduces the spreading of species due to mechanical mixing ( $\nabla \cdot (\mathbf{u}c_i)$ ) as well as from diffusion and volatilization to the gas phase. The tensor is denoted  $D_D$  (SI unit: m<sup>2</sup>/s) and the effective diffusion by  $D_e$  (SI unit: m<sup>2</sup>/s).

The last two terms on the right-hand side of Equation 4-11 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.

In order to solve for the solute concentration of species  $i$ ,  $c_i$ , the solute mass sorbed to solids  $c_{P,i}$  and dissolved in the gas-phase  $c_{G,i}$  are assumed to be functions of  $c_i$ . Expanding the time-dependent terms gives

$$\begin{aligned} \frac{\partial}{\partial t}(\theta c_i) + \frac{\partial}{\partial t}(\rho_b c_{P,i}) + \frac{\partial}{\partial t}(\alpha_v c_{G,i}) = & \\ (\theta + \rho_b k_{P,i} + \alpha_v k_{G,i}) \frac{\partial c_i}{\partial t} + (1 - k_{G,i}) c_i \frac{\partial \theta}{\partial t} - (\rho_P c_{P,i} - k_{G,i} c_i) \frac{\partial \epsilon_p}{\partial t} & \end{aligned} \quad (4-12)$$

where  $k_{P,i} = \partial c_{P,i} / \partial c_i$  is the adsorption isotherm and  $k_{G,i} = \partial c_{G,i} / \partial c_i$  is the linear volatilization. Equation 4-11 can then be written as

$$\begin{aligned} (\theta + \rho_b k_{P,i} + \alpha_v k_{G,i}) \frac{\partial c_i}{\partial t} + (1 - k_{G,i}) c_i \frac{\partial \theta}{\partial t} - (\rho_P c_{P,i} - k_{G,i} c_i) \frac{\partial \epsilon_p}{\partial t} + \mathbf{u} \cdot \nabla c_i & \\ = \nabla \cdot [(D_D + D_e) \nabla c_i] + R_i + S_i & \end{aligned} \quad (4-13)$$

### SATURATED POROUS MEDIA

In the case of transport in a saturated porous medium,  $\theta = \epsilon_p$  and the governing equations are

$$\begin{aligned}
& (\epsilon_p + \rho_b k_{P,i}) \frac{\partial c_i}{\partial t} + (c_i - \rho_P c_{P,i}) \frac{\partial \epsilon_p}{\partial t} + \mathbf{u} \cdot \nabla c_i = \\
& \nabla \cdot [(D_{D,i} + \theta \tau_{F,i} D_{F,i}) \nabla c_i] + R_i + S_i
\end{aligned} \tag{4-14}$$

### Convection

---

Convection 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:

$$\begin{aligned}
\mathbf{u}_a &= \frac{\mathbf{u}}{\epsilon_p} && \text{Saturated} \\
\mathbf{u}_a &= \frac{\mathbf{u}}{\theta} && \text{Partially saturated}
\end{aligned}$$

where  $\epsilon_p$  is the porosity and  $\theta = s\epsilon_p$  the liquid volume fraction, and  $s$  the saturation, a dimensionless number between 0 and 1.

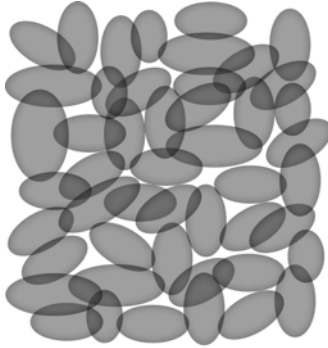


Figure 4-1: A block of a porous medium consisting of solids and the pore space between the solid grains. The average linear velocity describes how fast the fluid moves within the pores. The Darcy velocity attributes this flow over the entire fluid-solid face.

### 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 4-11 is written as:

$$\frac{\partial}{\partial t}(\theta c_i) + \frac{\partial}{\partial t}(\rho_b c_{P,i}) + \frac{\partial}{\partial t}(a_v c_{G,i}) + \nabla \cdot \mathbf{u} c_i = \nabla \cdot [(D_{D,i} + D_{e,i}) \nabla c_i] + R_i + S_i \quad (4-15)$$

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 non-conservative formulation described in Equation 4-11.

When using the non-conservative formulation, which is the default, the fluid is assumed incompressible and divergence free:  $\nabla \cdot \mathbf{u} = 0$ . The non-conservative 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 **Non-conservative form** (the default) or **Conservative form**. The conservative formulation should be used for compressible flow.



## Diffusion

---

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:

$$D_e = D_L \quad \text{Free Flow}$$

$$D_e = \frac{\epsilon_p}{\tau_L} D_L \quad \text{Saturated Porous Media}$$

$$D_e = \frac{\theta}{\tau_L} D_L \quad \text{Partially Saturated Porous Media}$$

$$D_e = \frac{\theta}{\tau_L} D_L + \frac{\alpha_v}{\tau_G} k_G D_G \quad \text{Partially Saturated with Volatilization}$$

Here  $D_L$  and  $D_G$  are the single-phase diffusion coefficients for the species diluted in pure liquid and gas phases respectively (SI unit:  $\text{m}^2/\text{s}$ ), and  $\tau_L$  and  $\tau_G$  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):

$$\tau_F = \theta^{-7/3} \epsilon^2, \quad \tau_G = \alpha_v^{-7/3} \epsilon^2$$

and Bruggeman model

$$\tau_F = \theta^{-5/2} \epsilon^2, \quad \tau_G = \alpha_v^{-5/2} \epsilon^2$$

For saturated porous media  $\theta = \epsilon_p$ . The fluid tortuosity for the Millington and Quirk model is

$$\tau_F = \epsilon_p^{-1/3}$$

and for the Bruggeman model the tortuosity is defined as

$$\tau_F = \epsilon_p^{-1/2}$$

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.

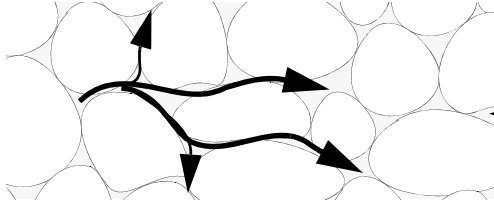


Figure 4-2: Spreading of fluid around solid particles in a porous medium.

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):

$$D_{Dii} = \alpha_L \frac{u_i^2}{|\mathbf{u}|} + \alpha_T \frac{u_j^2}{|\mathbf{u}|}$$
$$D_{Dij} = D_{Dji} = (\alpha_L - \alpha_T) \frac{u_i u_j}{|\mathbf{u}|}$$

In these equations,  $D_{Dii}$  (SI unit:  $\text{m}^2/\text{s}$ ) are the principal components of the dispersivity tensor, and  $D_{Dji}$  and  $D_{Dij}$  are the cross terms. The parameters  $\alpha_L$  and  $\alpha_T$  (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:

$$\begin{aligned}
 D_{Lxx} &= \alpha_1 \frac{u^2}{|\mathbf{u}|} + \alpha_2 \frac{v^2}{|\mathbf{u}|} + \alpha_3 \frac{w^2}{|\mathbf{u}|} \\
 D_{Lyy} &= \alpha_1 \frac{v^2}{|\mathbf{u}|} + \alpha_2 \frac{u^2}{|\mathbf{u}|} + \alpha_3 \frac{w^2}{|\mathbf{u}|} \\
 D_{Lzz} &= \alpha_1 \frac{w^2}{|\mathbf{u}|} + \alpha_3 \frac{u^2}{|\mathbf{u}|} + \alpha_3 \frac{v^2}{|\mathbf{u}|} \\
 D_{Lxy} &= D_{Lyx} = (\alpha_1 - \alpha_2) \frac{uv}{|\mathbf{u}|} \\
 D_{Lxz} &= D_{Lzx} = (\alpha_1 - \alpha_3) \frac{uw}{|\mathbf{u}|} \\
 D_{Lyz} &= D_{Lzy} = (\alpha_1 - \alpha_3) \frac{vw}{|\mathbf{u}|}
 \end{aligned} \tag{4-16}$$

In Equation 4-16 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  $\alpha_1$  (SI unit: m) is the longitudinal dispersivity. If  $z$  is the vertical axis,  $\alpha_2$  and  $\alpha_3$  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 physics interface predefines three relationships to predict the solid concentrations,  $c_{p_i}$  from the concentration in the liquid phase,  $c_i$ :

$$\begin{aligned}
c_P &= K_P c & \frac{\partial c_P}{\partial c} &= \frac{\partial}{\partial c}(K_P c) & \text{User defined} \\
c_P &= K_F c^N & \frac{\partial c_P}{\partial c} &= N K_F c^{N-1} & \text{Freundlich (Ref. 3)} \\
c_P &= \frac{K_L c_{P\max} c}{1 + K_L c} & \frac{\partial c_P}{\partial c} &= \frac{K_L c_{P\max}}{(1 + K_L c)^2} & \text{Langmuir (Ref. 4, Ref. 5)}
\end{aligned} \tag{4-17}$$

The above equations contains the following parameters:

- User defined isotherm  $K_P$  (dimensionless)
- Freundlich exponent  $N$  (dimensionless), Freundlich constant  $K_F$  (SI unit  $\text{m}^{3N} \cdot \text{mol}^{(1-N)}/\text{kg}$ ).
- Langmuir: maximum  $c_{P\max}$  (SI unit  $\text{mol}/\text{m}^3$ ), Langmuir constant  $K_L$  (SI unit  $\text{m}^3/\text{mol}$ ).

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. In COMSOL Multiphysics, arbitrary expressions can be entered to define, for example, non-equilibrium and temperature-dependent adsorption laws, including those set out by Fetter (Ref. 7) and Bear and Verruijt (Ref. 8).

The retardation factor,  $\mathbf{RF}$ , describes how adsorption slows the solute velocity,  $\mathbf{u}_c$ , relative to the average linear velocity of the fluid,  $\mathbf{u}_a$ , as in

$$\mathbf{RF} = 1 + \frac{\rho_b}{\theta} \frac{\partial c_P}{\partial c} = \frac{\mathbf{u}_a}{\mathbf{u}_c}$$

If the contaminant moves at the average linear velocity of the fluid for  $\mathbf{RF} = 1$ . For  $\mathbf{RF} > 1$ , the contaminant velocity is smaller than the fluid velocity owing to residence time on solids.

### *Reactions*

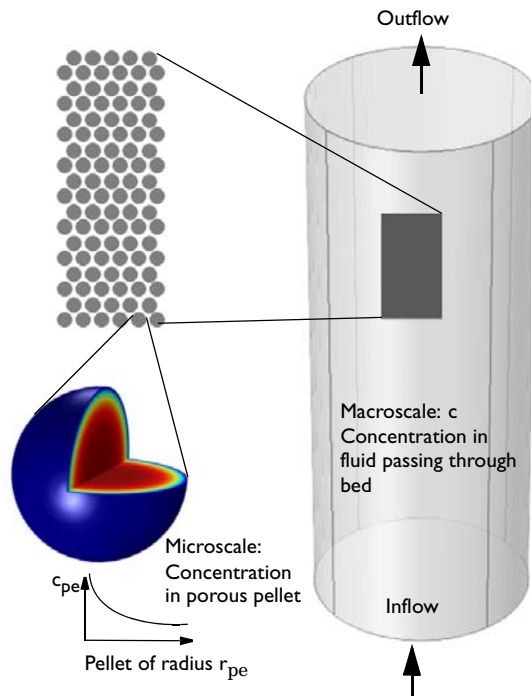
Chemical reactions of all types influence species transport in porous media. Examples include biodegradation, radioactive decay, transformation to tracked products, temperature- and pressure-dependent functions, exothermic reactions, and endothermic reactions. The reactions represent change in species 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  $\theta$ . Similarly, solid phase reaction expressions include the bulk density,  $\rho_b$ , and gas phase reactions include the gas volume fraction,  $\alpha_v$ .

### *Theory for the Reactive Pellet Bed*

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The feature Reactive Pellet Bed, available to users of the Chemical Reaction Engineering Module, adds to the transport of diluted species interface a domain feature that can simulate regions filled with spherical reactive catalyst pellets, as in packed bed reactors. The pellets are simulated with the Extra Dimension technology provided by COMSOL: A 1D, 2D, or 3D domain comprises the bed volume. The extra dimension is the added radial microscale dimension inside each pellet.



*Figure 4-3: Schematic showing the macroscale (bed volume) and the microscale (pellet)*

The transport and reaction equations inside the pellets is done with an extra dimension feature attached to the 1D, 2D, or 3D physics interfaces, including axisymmetric cases.

The equations inside the spherical pellet are solved as a spherical transport equations on a non-dimensional radial coordinate on the domain 0-1. Different pellet radii and even uneven radius distributions can be used.

The model equations assume spherical particles of a radius  $r_{pe}$ . Consider the microscale concentration  $c_{pe}$  inside an individual porous pellet or particle, and the macro-concentration  $c$  in the packed bed gas volume.

The pellet radius input can be:

- one uniform pellet radius, that can be space dependent  $f(x, y, z)$ ,
- binary, ternary, and so on, mix up to 5 radii. The user inputs a table with the mix of sizes (1 mm, 2 mm, for example), and a percentage of each. Different chemical reactions per pellet size can be specified.

The model equation for the bulk (macroscale) species is, for example:

$$\epsilon_b \frac{\partial}{\partial t}(c_i) + \mathbf{u} \cdot \nabla c_i + \nabla \cdot (-D_{b,i} \nabla c_i) = R_i \quad (4-18)$$

- The dependent variable  $c$  for each chemical species  $i$  represents the interstitial concentration (SI unit: mol/m<sup>3</sup>), that is, the physical concentration based on unit volume of fluid flowing between the pellets.
- $\epsilon_b$  is the bed porosity (SI unit: 1). It should be noted that the  $R$  term on the right hand side is per unit volume of bed, (SI unit: mol/(m<sup>3</sup> · s)).

Looking inside a pellet: Assuming no concentration variations in the space-angle ( $\theta, \varphi$ ) direction, but only in the radial ( $r$ ) direction of the spherical particle allows a spherically symmetric reaction-diffusion transport equation inside the pellet. If  $r_{dim}$  (SI unit: m) is the spatial radial coordinate in the pellet, and  $r_{pe}$  is the pellet radius, the non-dimensional coordinate  $r=r_{dim}/r_{pe}$  can be defined. The modeling domain on  $r$  goes from 0 to 1.

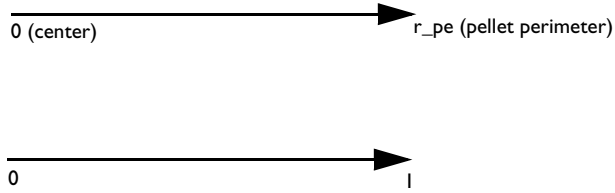


Figure 4-4: Modeling domain in a pellet for a dimensional coordinate (top) and non-dimensional coordinate (bottom.)

A shell mole balance across a spherical shell at radius  $r_{\text{dim}}$  (SI unit: m), and a subsequent variable substitution  $r = r_{\text{dim}}/r_{\text{pe}}$  gives the following governing equation inside the pellet on the domain  $0 < r < 1$ :

$$4\pi N \left\{ r^2 r_{\text{pe}}^2 \epsilon_{\text{pc}} \frac{\partial}{\partial t} (c_{\text{pc}, i}) + \nabla \cdot (-r^2 D_{\text{pc}, i} \nabla c_{\text{pc}, i}) = r^2 r_{\text{pe}}^2 R_{\text{pc}, i} \right\} \quad (4-19)$$

where

- $N$  is the number of pellets per unit volume of bed.
- Equally as in Equation 4-18,  $c_{\text{pc}}$  is the interstitial (physical) species concentration in moles/m<sup>3</sup> fluid volume element inside the pore channel,
- $R_{\text{pc}}$  is the reaction rate in moles/(m<sup>3</sup> · s) of particle volume. It should be stressed that the user input of  $R$  is per unit volume of pellet.

The effective diffusion coefficient in Equation 4-18 and Equation 4-19 depend on the porosity  $\epsilon_{\text{pc}}$ , tortuosity  $\tau$  and the physical gas diffusivity  $D$  of in the porous particle generally as

$$D_{\text{pc}} = \frac{\epsilon_{\text{pc}} D}{\tau}.$$

The available tortuosity models for porous media are the Millington and Quirk (Ref. 12),

$$\tau = \epsilon_{\text{pc}}^{-1/3} \Rightarrow D_{\text{pc}} = \epsilon_{\text{pc}}^{4/3} D, \quad (4-20)$$

Bruggemann,

$$\tau = \varepsilon_{\text{pc}}^{-1/2} \Rightarrow D_{\text{pc}} = \varepsilon_{\text{pc}}^{3/2} D \quad (4-21)$$

and the Tortuosity model, where the tortuosity expression is entered as user input:

$$D_{\text{pc}} = \frac{\varepsilon_{\text{pc}} D}{\tau} \quad (4-22)$$

These are readily used for both gaseous and liquid fluids along with various types of particle shapes. For instance, the first model has been shown to fit mass transport in soil-vapor and soil-moisture well.

Equation 4-18 can be solved for two types of boundary conditions at the interface between the pellet surface and the fluid in this feature.

- **Continuous concentrations:** assuming that all resistance to mass transfer is within the pellet and no resistance to pellet-fluid mass transfer on bulk fluid side. The concentration in the fluid will thus be equal to that in the pellet pore just at the pellet surface:  $c_{\text{pc},i} = c_i$ . This constraint also automatically ensures flux continuity between the pellet system and the free fluid system though 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. The resistance is expressed in terms of a film mass transfer coefficient,  $h_{D,i}$ , such that:

$$N_{i,\text{inward}} = h_{D,i}(c_{ii} - c_{\text{pc},i}), \quad (4-23)$$

where  $N_{i,\text{inward}}$  is the molar flux from the free fluid into a pellet and has the unit moles/(m<sup>2</sup> · s).

With the film resistance formulation, the free fluid Equation 4-18 needs to be amended for flux continuity so that

$$\varepsilon_b \frac{\partial}{\partial t}(c_i) + \mathbf{u} \cdot \nabla c_i + \nabla \cdot (-D_{b,i} \nabla c_i) = R_i - N_{i,\text{inward}} S_b \quad (4-24)$$

where  $S_b$  (SI unit: m<sup>2</sup>/m<sup>3</sup>) is the specific surface area exposed to the free fluid of the packed bed (not including the inside of the pores).

For the case of randomly packed spherical particles, the specific surface area exposed to the free fluid is (Ref. 3):

$$S_b = \frac{3}{r_{\text{pc}}}(1 - \varepsilon_b) \quad (4-25)$$



The mass transfer coefficient in Equation 4-23 can be computed from the fluid properties and flow characteristics within the porous media. For this, the Sherwood,  $Sh$ , number defined as the ratio between the convective mass transfer coefficient and the diffusive mass transfer coefficient is often used:

$$Sh = \frac{hL}{D}$$

where  $L$  is a characteristic length (for spheres typically the radius) and  $D$  the diffusion coefficient in the fluid. From the Sherwood number definition, the mass transfer coefficient can be computed.

Three commonly used empirical expressions for the calculation of the Sherwood number are the Frössling relation (Ref. 4):

$$Sh = 2 + 0,552Re^{1/2}Sc^{1/3}, \quad (4-26)$$

which was measured on particles in the size region 1 mm, the Rosner relation (Ref. 5)

$$Sh = Sc^{0,4}(0,4Re^{1/2} + 0,2Re^{2/3}), \quad (4-27)$$

and the Garner and Key relation (Ref. 4)

$$Sh = 0,94Re^{1/2}Sc^{1/3}, \quad (4-28)$$

which was measured for  $Re$  numbers greater than 250.

All three depend on the Reynolds,  $Re$ , and Schmidt,  $Sc$ , numbers. The first describing the fluid flow regime (laminar vs turbulent) and the second, the ratio between the viscous diffusion rate and the molecular (mass) diffusion rate. In the expressions, properties such as velocity,  $u$ , dynamic viscosity,  $\mu$ , and density,  $\rho$ , of the fluid are included.

$$Re = \frac{\rho u L}{\mu}$$

$$Sc = \frac{\mu}{\rho D}$$

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# Theory for the Electrophoretic Transport Interface

The [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,  $c_i$  (mol/m<sup>3</sup>), and the potential,  $\phi_l$  (V).

The species are transported by diffusion, migration, and (optionally) convection according to the Nernst-Planck set of equations. The flux of species  $i$  is denoted  $\mathbf{N}_i$  (mol/(m<sup>2</sup>s)) according to

$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_l + \mathbf{u} c_i \quad (4-29)$$

where  $D_i$  (m<sup>2</sup>/s) is the diffusion coefficient,  $z_i$  (1) the corresponding charge,  $u_{m,i}$  (s·mol/kg) the mobility and  $\mathbf{u}$  (m/s) the velocity vector. 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<sup>2</sup>), is defined as

$$\mathbf{i}_l = \sum_i z_i \mathbf{N}_i \quad (4-30)$$

where the summation is made over all species in the electrolyte.

The governing equation for the electrolyte potential is

$$\nabla \cdot \mathbf{i}_l = Q_l \quad (4-31)$$

where  $Q_l$  (A/m<sup>3</sup>) 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

$$\sum_{i=1}^{N+2} z_i c_i = 0 \quad (4-32)$$

In water-based systems the species H<sup>+</sup> and OH<sup>-</sup> are always present. The auto ionization reaction for water is



This reaction is fast, following the equilibrium relation

$$c_{\text{H}^+} \cdot c_{\text{OH}^-} = K_w \times 1 \text{ mol}^2 \text{ dm}^{-6} \quad (4-34)$$

where  $K_w \approx 10^{-14}$ .

Now, the electroneutrality condition, including the two additional species H<sup>+</sup> and OH<sup>-</sup>, reads

$$c_{\text{H}^+} - c_{\text{OH}^-} + \sum_{i=1}^N z_i c_i = 0 \quad (4-35)$$

Combining these two equations results in the following algebraic expressions for the concentrations of H<sup>+</sup> and OH<sup>-</sup>.

$$c_{\text{H}^+} = -\frac{\Sigma}{2} + \sqrt{\frac{\Sigma^2}{4} + K_w \times 1 \text{ mol}^2 \text{ dm}^{-6}} \quad (4-36)$$

and

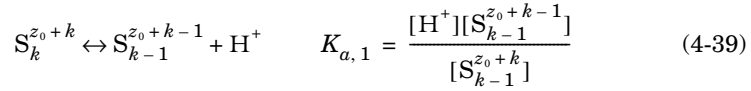
$$c_{\text{OH}^-} = \frac{\Sigma}{2} + \sqrt{\frac{\Sigma^2}{4} + K_w \times 1 \text{ mol}^2 \text{ dm}^{-6}} \quad (4-37)$$

where

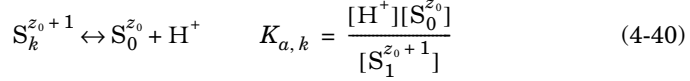
$$\Sigma = \sum_{i=1}^N z_i c_i \quad (4-38)$$

### MASS BALANCE EQUATIONS FOR DISSOCIATION SPECIES

Assume a set of species S<sub>i</sub> describing *k* dissociation steps from



to



where  $z_0$  is the charge (valence) of species  $S_0$  (which has no dissociable protons) and  $K_{a,j}$  is the acid (equilibrium) constant of the  $j$ :th dissociation reaction. The brackets [ ] here represents the species activity. The charge of each species is always deductible from the index  $i$  according to  $z_{0+i}$  and will be dropped from now on.

If the proton activity is known, any species  $S_m$  may be expressed using any other species  $S_l$  according to

$$[S_m] = \frac{[H]^{m-l}[S_l]}{\prod_{j=k-m+1}^{k-l} K_{a,j}} \quad (4-41)$$

if  $m > l$  and

$$[S_m] = [H]^{m-l}[S_l] \prod_{j=k-l+1}^{k-m} K_{a,j} \quad (4-42)$$

if  $l < m$ .

Setting  $m=i$  and denoting the flux of species  $i$  by  $\mathbf{N}_i$  using equation Equation 4-29, the mass balance equation for the concentration  $c_i$  of each subspecies  $i$  in the dissociation chain is

$$\frac{\delta c_i}{\delta t} + \nabla \cdot \mathbf{N}_i = R_{\text{eq},i,k-i} - R_{\text{eq},i,k-i+1} + R_i \quad (4-43)$$

where  $R_{\text{eq},i,j}$  is the reaction source stemming from the  $j$ :th dissociation step (with  $R_{\text{eq},i,k+l}=0$ ), and  $R_i$  any additional reaction sources.

The reaction source contributions from the dissociation steps are generally not known, but may be cancelled by taking the sum of all mass balance equations, resulting in

$$\sum_{i=0}^k \left( \frac{\delta c_i}{\delta t} + \nabla \cdot \mathbf{N}_i \right) = \sum_{i=0}^k R_i \quad (4-44)$$

### 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  $\bar{v}$  (1) removed from the molecule.  $\bar{v}$  is typically provided as a function of pH, based on experimental data. The average charge of the species then is  $\bar{z} = z_0 - \bar{v}$ , so that the flux of the species is written as:

$$\mathbf{N}_i = -D\nabla c_i - \bar{z}u_m F c_i \nabla \phi_l + \mathbf{u}c_i \quad (4-45)$$

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,  $\bar{z}^2 = (z_0 - \bar{v})^2$ , is not equal to the “average squared charge”,  $\overline{z^2} = z_0^2 + 2z_0\bar{v} + \bar{v}^2 = \bar{z}^2 - \bar{v}^2 + \bar{v}^2$  (Ref. 1).

The addition to the current density vector is

$$\mathbf{i}_l = \dots - F(\bar{z}D_i \nabla c_i + \overline{z^2}u_m c_i \nabla \phi_l) \quad (4-46)$$

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

$$\overline{v^2} = -c_{H^+} \frac{d}{dc_{H^+}} \bar{v} + \bar{v}^2 \quad (4-47)$$

And from this one can derive the average squared charge according to

$$\overline{z^2} = -c_{H^+} \frac{d}{dc_{H^+}} \bar{v} + \bar{z}^2 = -c_{H^+} \frac{d}{dc_{H^+}} \bar{z} + \bar{z}^2 \quad (4-48)$$

### DIFFUSIVITY-MOBILITY RELATIONS

The Stokes radius  $r$  of a molecule is related to the diffusivity according to

$$r = \frac{kT}{6\pi\mu D} \quad (4-49)$$

where  $\mu$  (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

$$u_m = \frac{D}{RT} \quad (4-50)$$

For larger molecules, such as proteins, the mobility may instead be calculated based on the Debye-Hückel-Henry expression (Ref. 2) according to

$$u_m = \frac{ef(\kappa r)}{6\pi\mu F(1 + \kappa r)} = \frac{Df(\kappa r)}{RT(1 + \kappa r)} \quad (4-51)$$

where  $\kappa$  (1/m) is the Debye parameter, which depends on the ionic strength of the solution, is defined for ideal solutions as

$$\kappa^2 = \frac{2e^2 N_A}{\epsilon\epsilon_0 kT} \sum_{i=1}^N z_i^2 c_i \quad (4-52)$$

where  $\epsilon$  is the dielectric constant of the fluid and  $\epsilon_0$  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  $r \rightarrow 0$ .

For larger molecules (macro ions), where the distance between the charges is large compared to  $1/\kappa$ , the Linderström-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

$$\kappa^2 = \frac{2e^2 N_A}{\epsilon\epsilon_0 kT} \left( \sum_{i=1}^{N-M} z_i^2 c_i + \sum_{i=N-M+1}^N \text{abs}(z_i) c_i \right) \quad (4-53)$$

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# 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<sup>2</sup>), referring to species adsorbed on a reactive surface, and an arbitrary number of bulk concentrations  $c_{b,k}$  (SI unit: mol/m<sup>3</sup>), 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*

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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<sup>2</sup>/s) is the surface diffusion coefficient for species  $i$ .

The governing equation for the surface concentrations is written as:

$$\frac{\partial c_{s,i}}{\partial t} = -\nabla_t \cdot \mathbf{N}_{t,i} + R_{s,i} \quad (4-54)$$

where  $R_{s,i}$  (SI unit: mol/(m<sup>2</sup>·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,  $\theta_i$  (dimensionless), of the species (with index  $i$ ).

Writing the density of sites of the surface as  $\Gamma_s$  (SI unit: mol/m<sup>2</sup>) and the site occupancy number for each species as  $\sigma_i$  (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,  $\theta_*$ , can be calculated from:

$$\theta_* = 1 - \sum_i \theta_i$$

### *Governing Equations for the Bulk Concentrations*

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#### **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<sup>2</sup>)).

The reaction rate in mass basis,  $r_{b,k}$  (SI unit: kg/(s·m<sup>2</sup>)) 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  $\rho_k$  is the species density (SI unit: kg/m<sup>3</sup>).

#### **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.

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### 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<sup>2</sup>), for species  $k$  is governed by the equation:

$$\frac{\partial c_{b, k}}{\partial t} = R_{b, k} \quad (4-55)$$

The bulk concentration in mass basis,  $m_{b,k}$  (SI unit: kg/m<sup>2</sup>) 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<sup>2</sup>) is

$$m_{b,\text{tot}} = \sum_k m_{b,k}$$

and the total bulk thickness,  $s_{\text{tot}}$  (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*

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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*

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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 regards 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 4-54](#) and [Equation 4-55](#), respectively.

$$-c_{s,i} \frac{\partial}{\partial t} \ln \partial A$$

$$-c_{b,k} \frac{\partial}{\partial t} \ln \partial A$$

where  $\partial A$  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 4-54](#) and [Equation 4-55](#), respectively:

$$\nabla_t \cdot (c_{s,i} \mathbf{v}_{t, \text{mesh}})$$

$$\nabla_t \cdot (c_{b,k} \mathbf{v}_{t, \text{mesh}})$$

where  $\mathbf{v}_{t,\text{mesh}}$  is the mesh velocity in the tangential direction.

This convective term needs often to be stabilized using methods such as streamline diffusion or isotropic diffusion.

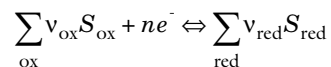
### *Reference for the Surface Reactions Interface*

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I. 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



is used to define the stoichiometric coefficients,  $\nu_i$ , with  $\nu_i$  being positive ( $\nu_{\text{red}}$ ) for products and negative ( $\nu_{\text{ox}}$ ) 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*

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The molar species fluxes,  $N_i$  (SI unit: mol/(m<sup>2</sup>·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:

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

where  $i_m$  is the local current density (SI unit: A/m<sup>2</sup>) 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:  $\text{m}^2/\text{m}^3$ ) is the specific surface area.

### *Mass Sources and Sinks*

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To compute the mass flux of a species,  $\mathbf{n}_i$  (SI unit:  $\text{kg}/(\text{m}^2 \cdot \text{s})$ ), the molar flux is multiplied by the molar mass,  $M_i$  (SI unit:  $\text{kg}/\text{mol}$ ), 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.





# Fluid Flow Interfaces

This chapter describes the physics interfaces found under the **Fluid Flow>Porous Media and Subsurface 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 Darcy's Law Interface](#)
- [The Free and Porous Media Flow Interface](#)
- [The Brinkman Equations Interface](#)
- [Theory for the Darcy's Law Interface](#)
- [Theory for the Free and Porous Media Flow Interface](#)
- [Theory for the Brinkman Equations Interface](#)
- [Theory for the Coupling of Fluid Flow to Electrochemical Reactions](#)

# The Darcy's Law Interface

The **Darcy's Law (dl)** interface (  ), found under the **Porous Media and Subsurface Flow** branch (  ) when adding a physics interface, is used to simulate fluid flow through interstices in a porous medium. It can be used to model low-velocity flows or media where the permeability and porosity are very small, and for which the pressure gradient is the major driving force and the flow is mostly influenced by the frictional resistance within the pores. Set up multiple **Darcy's Law** interfaces to model multiphase flows involving more than one mobile phase. The Darcy's Law interface can be used for stationary and time-dependent analyses.

The main feature is the 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**  $p_{\text{ref}}$  (SI unit: Pa). The default value is `1[atm]`.

## 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.

## DISCRETIZATION

To display this section, click the **Show** button (  ) and select **Discretization**.

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

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

For details about the boundary fluxes settings, see [Computing Accurate Fluxes](#) in the COMSOL Multiphysics Reference Manual.

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



- [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*
- 

### *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 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.



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 2-3](#) for links to common sections and [Table 2-4](#) to common feature nodes. You can also search for information: press F1 to open the **Help** window or Ctrl+F1 to open the **Documentation** window.

## DOMAIN

- [Fluid and Matrix Properties](#)
- [Initial Values](#)
- [Mass Source](#)

## BOUNDARY, EDGE, AND POINT

The following nodes (listed in alphabetical order) are available on exterior boundaries:

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.

## Fluid and Matrix Properties

---

The **Fluid and Matrix Properties** node adds the equations for Darcy’s law, [Equation 5-1](#) and [Equation 5-2](#)(excluding any mass sources), and contains settings for the fluid properties and the porous matrix properties such as the effective porosity.

$$\frac{\partial}{\partial t}(\rho\varepsilon) + \nabla \cdot (\rho\mathbf{u}) = Q_m \quad (5-1)$$

$$\mathbf{u} = -\frac{\kappa}{\mu}\nabla p \quad (5-2)$$

### 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**  $\rho$  (SI unit: kg/m<sup>3</sup>) uses values **From material** based on the **Fluid material** selection.

- For **User defined** enter another value or expression. The default is 0 kg/m<sup>3</sup>.
- 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**  $\mu$  (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.

### 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**  $\varepsilon_p$  (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.

The default **Permeability**  $\kappa$  (SI unit:  $\text{m}^2$ ) uses the value **From material**, as defined by the **Porous material** selected. For **User defined** select **Isotropic** to define a scalar value or **Diagonal, Symmetric**, or **Anisotropic** to define a tensor value and enter another value or expression in the field or matrix.

### *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 5-8, the equation for porosity).

$$\frac{\partial}{\partial t}(\rho\varepsilon) + \nabla \cdot (\rho\mathbf{u}) = Q_m \quad (5-3)$$

#### **MASS SOURCE**

Enter a value or expression for the **Mass source**  $Q_m$  (SI unit:  $\text{kg}/(\text{m}^3 \cdot \text{s})$ ). The default is  $0 \text{ kg}/(\text{m}^3 \cdot \text{s})$ .

### *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.

#### **INITIAL VALUES**

Enter a value or expression for the initial value of the **Pressure**  $p$  (SI unit: Pa). The default value is 0 Pa.


### *Porous Electrode Coupling*

---

Use the **Porous Electrode Coupling** node to define a mass source based on the volumetric current densities of one or multiple **Porous Electrode Reaction** nodes in an Electrochemistry interface.

The source (or sink) is proportional to the **Molar mass (kg/mol)** of the reacting species, the current densities and the stoichiometric coefficients according to Faraday's law as defined by summation over the Reaction Coefficient subnodes.

#### **SPECIES**

Based on the number of species required for the model, use the **Add** ( **+** ) and **Delete** (  ) buttons under the table to add or remove **Species**. Then enter a value for the **Molar mass (kg/mol)** in the applicable rows for each species.

The setting in the table will determine the number of available fields for entering the stoichiometric coefficients of the Reaction Coefficient subnodes.



### *Electrode Surface Coupling*

---

Use the **Electrode Surface Coupling** node to define a combined wall and inflow/outflow boundary condition based on current densities of one or multiple Electrode Reaction nodes in an Electrochemistry interface.

The flow is proportional to the **Molar mass (kg/mol)** of the reacting species, the current densities and the stoichiometric coefficients according to Faraday's law as defined by summation over the Reaction Coefficient subnodes.

#### **SPECIES**

Based on the number of species required for the model, use the **Add** (  ) and **Delete** (  ) buttons under the table to add or remove **Species**. Then enter a value for the **Molar mass (kg/mol)** in the applicable rows for each species.

The setting in the table will determine the number of available field for entering the stoichiometric coefficients of the Reaction Coefficient subnodes.

### *Pressure*


---

Use the **Pressure** node to specify the pressure on a boundary. In many cases the distribution of pressure is known, giving a Dirichlet condition  $p = p_0$  where  $p_0$  is a known pressure given as a number, a distribution, or an expression involving time,  $t$ , for example.

#### **PRESSURE**

Enter a value or expression for the **Pressure**  $p_0$ (SI unit: Pa). Enter a relative pressure value in  $p_0$  (SI unit: Pa).

#### **CONSTRAINT SETTINGS**

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

### *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:

$$\mathbf{n} \cdot \rho \frac{\kappa}{\mu} \nabla p = N_0$$

where  $N_0$  is a value or expression for the specified inward (or outward) Darcy flux.

### 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<sup>2</sup>·s)), **Edges** (SI unit: kg/(m·s)), and **Points** (SI unit: kg/s)).

### *Inlet*

---

The **Inlet** node adds a boundary condition for the inflow (or outflow) perpendicular (normal) to the boundary:

$$\mathbf{n} \cdot \rho \frac{\kappa}{\mu} \nabla p = \rho U_0$$

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.

### INLET

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.

### *Symmetry*

---

The **Symmetry** node describes a symmetry boundary. The following condition implements the symmetry condition on an axis or a flow divide:

$$\mathbf{n} \cdot \frac{\kappa}{\mu} \nabla p = 0$$

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 impervious boundaries. The mathematical formulation is:

$$\mathbf{n} \cdot \rho \frac{\kappa}{\mu} \nabla p = 0$$

where  $\mathbf{n}$  is the vector normal to the boundary.

### *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,  $\rho$  is the fluid density,  $\mathbf{u}_1$  and  $\mathbf{u}_2$  are the Darcy's velocities in the adjacent domains (as defined in [Equation 5-7](#)) and  $N_0$  is a specified value or expression for the flux discontinuity.

$$\mathbf{u} = -\frac{\kappa}{\mu} \nabla p \tag{5-4}$$

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:  $\text{kg}/(\text{m}^2 \cdot \text{s})$ ). 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:



$$-\mathbf{n} \cdot \rho \frac{\kappa}{\mu} \nabla p = \rho U_0$$

where  $U_0$  is a specified value or expression for the outward (or inward) Darcy velocity. A positive value of the velocity  $U_0$  corresponds to flow out of the model domain whereas a negative value represents an inflow.

#### **OUTLET**

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.

# The Free and Porous Media Flow Interface

The **Free and Porous Media Flow (fp)** 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 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 **Porous 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 (non-isothermal 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 in free flow (Stokes flow)** check box if the inertial forces are small compared to the viscous forces.

Select the **Neglect inertial term in porous media flow (Stokes-Brinkman)** check box to model flow at very low Reynolds numbers in the porous media, for which the inertial term in the Brinkman equations can be neglected. The physics interface then solves the linear Stokes-Brinkman equations.

#### *Reference Pressure Level*

Enter a **Reference pressure level**  $p_{\text{ref}}$  (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  $\mathbf{u}$**  (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
- Forchheimer Drag
- Initial Values
- Mass Source
- Porous Electrode Coupling
- Porous Matrix Properties
- Volume Force
- Wall



See the Transport of Diluted Species interface for [Porous Electrode Coupling](#) and [Reaction Coefficients](#).

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 2-3](#) for links to common sections and [Table 2-4](#) 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**  $\rho$  (SI unit:  $\text{kg}/\text{m}^3$ ) uses values **From material** based on the **Fluid material** selection. For **User defined** enter another value or expression. The default is  $0 \text{ kg}/\text{m}^3$ .

The **Dynamic viscosity**  $\mu$  (SI unit:  $\text{Pa}\cdot\text{s}$ ) uses values **From material** based on the **Fluid material** selection. For **User defined** enter another value or expression. The default is  $0 \text{ Pa}\cdot\text{s}$ .

### *Porous Matrix Properties*

---

Use the **Porous 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. The **Forchheimer Drag** subnode is available from the context menu (right-click the parent node) or from the **Physics** toolbar, **Attributes** menu.

#### **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** (the material defined for the domain) for the porous matrix. Select another material as needed.

##### *Porosity*

The default **Porosity**  $\varepsilon_p$  (a dimensionless number between 0 and 1) uses values **From material** as defined by the **Porous material** selection. For **User defined** enter another value or expression. The default is 0.

##### *Permeability*

The default **Permeability**  $\kappa_{br}$  (SI unit:  $\text{m}^2$ ) uses values **From material** as defined by the **Porous material** selection. For **User defined** select **Isotropic**, **Diagonal**, **Symmetric**, or **Anisotropic** from the list and then enter other values or expressions. The components of a permeability in the case that it is a tensor ( $\kappa_{xx}$ ,  $\kappa_{yy}$ , and so on, representing an anisotropic permeability) are available as `fp.kappaxx`, `fp.kappayy`, and so on (using the default name `fp`). The default is  $0 \text{ m}^2$ .

### *Source Term*

Enter a value or expression for an optional mass source (or sink) **Source term**  $Q_{br}$  (SI unit:  $\text{kg}/(\text{m}^3 \cdot \text{s})$ ). This term accounts for mass deposit and mass creation within domains. The physics interface assumes that the mass exchange occurs at zero velocity.

### *Volume Force*

---

The **Volume Force** node specifies the force  $\mathbf{F}$  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**  $\mathbf{F}$  (SI unit:  $\text{N}/\text{m}^3$ ).

### *Forchheimer Drag*

---

The **Forchheimer Drag** subnode is available from the context menu (right-click the [Porous Matrix Properties](#) parent node) or from the **Physics** toolbar, **Attributes** menu. It can be used on the domain selection that corresponds to the porous medium. For the Brinkman equations the drag of the fluid on the porous matrix is proportional to the flow velocity, in the same way as for Darcy's law. Add a Forchheimer drag, proportional to the square of the fluid velocity, as needed.

#### **FORCHHEIMER DRAG**

Enter a value for the **Forchheimer coefficient**  $\beta_F$  (SI unit:  $\text{kg}/\text{m}^4$ ).


### *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  $\mathbf{u}$**  (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.

### BOUNDARY CONDITION

Select a **Boundary condition** for the wall.

- No Slip<sup>1</sup>
- Slip
- Sliding Wall
- Moving Wall
- Leaking Wall

#### No Slip

**No slip** is the default boundary condition for a stationary solid wall for laminar flow (and SST, Low Re k- $\epsilon$ , 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.

#### Sliding Wall

The **Sliding wall** boundary condition is appropriate if the wall behaves like a conveyor belt; that is, the surface is sliding in its tangential direction. A velocity is prescribed at the wall and the boundary itself does not have to actually move relative to the reference frame.

- For 3D components, values or expressions for the **Velocity of sliding wall**  $\mathbf{u}_w$  should be specified. If the velocity vector entered is not in the plane of the wall, COMSOL Multiphysics projects it onto the tangential direction. Its magnitude is adjusted to be the same as the magnitude of the vector entered.
- For 2D components, the tangential direction is unambiguously defined by the direction of the boundary. For this reason, the sliding wall boundary condition has

different definitions in different space dimensions. A single entry for the **Velocity of the tangentially moving wall**  $U_w$  should be specified in 2D.

- For 2D axisymmetric components when **Swirl flow** is selected in the physics interface properties, the **Velocity of moving wall**,  $\varphi$  **component**  $v_w$  may also be specified.

#### *Moving Wall*


For an arbitrary wall movement, the condition  $\mathbf{u} = \mathbf{u}_w$  may be prescribed. In this case, the components of the **Velocity of moving wall**  $\mathbf{u}_w$  should be specified.

Specifying this boundary condition 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.

#### *Leaking Wall*

This boundary condition may be used to simulate a wall where fluid is leaking into or leaving the domain with the velocity  $\mathbf{u} = \mathbf{u}_1$  through a perforated wall. The components of the **Fluid velocity**  $\mathbf{u}_1$  on the leaking wall should be specified.



### **CONSTRAINT SETTINGS**

This section is displayed by clicking the **Show** button (  ) and selecting **Advanced Physics Options**.



- [Moving Mesh Interface](#) in the *COMSOL Multiphysics Reference Manual*
-

# 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 2-3](#) 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.

## SETTINGS

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

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

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

## PHYSICAL MODEL

This node specifies the properties of the Brinkman Equations interface, which describe the overall type of fluid flow model.

### *Compressibility*

By default the physics interface uses the **Incompressible flow** formulation of the Brinkman equations to model constant density flow. Alternatively, select **Compressible flow (Ma<0.3)** from the **Compressibility** list if there are small variations in the density, typically dependent on the temperature (non-isothermal 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 very low Reynolds numbers for which the inertial term can be neglected in the Brinkman equations. 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**  $p_{\text{ref}}$  (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**  $\mathbf{u}$  (SI unit: m/s) and its components, and the **Pressure**  $p$  (SI unit: Pa).

## ADVANCED SETTINGS

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

- 
- [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](#)

---

### *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](#)
- [Forchheimer Drag](#)
- [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
- InletLine Mass Source
- Boundary Stress
- Outlet
- Open Boundary
- Periodic Flow Condition
- Point Mass Source
- Pressure Point ConstraintSymmetry
- Wall



In the *COMSOL Multiphysics Reference Manual* see [Table 2-3](#) for links to common sections and [Table 2-4](#) 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 5-10](#) and [Equation 5-11](#) (excluding any mass sources), and provides an interface for defining the properties of the fluid material and the porous matrix. The [Forchheimer Drag](#) subnode is available from the context menu (right-click the parent node) or from the **Physics** toolbar, **Attributes** menu.

#### **FLUID PROPERTIES**

The default **Fluid material** uses the **Domain material** (the material defined for the domain). Select another material as needed.

Both the default **Density**  $\rho$  (SI unit:  $\text{kg}/\text{m}^3$ ) and **Dynamic viscosity**  $\mu$  (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  $0 \text{ kg}/\text{m}^3$  for the density and  $0 \text{ Pa}\cdot\text{s}$  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 yoghurt, paper pulp, and polymer suspensions.

## POROUS MATRIX PROPERTIES

The default **Porous material** uses the **Domain material** (the material defined for the domain) for the porous matrix. Select another material as needed.

Both the default **Porosity**  $\epsilon_p$  (a dimensionless number between 0 and 1) and **Permeability**  $\kappa$  (SI unit:  $\text{m}^2$ ) use values **From material** as defined by the **Porous material** selection. For **User defined** select **Isotropic**, **Diagonal**, **Symmetric**, or **Anisotropic** based on the characteristics of the permeability, and enter another value or expression. The components of a permeability in the case that it is a tensor ( $\kappa_{xx}$ ,  $\kappa_{yy}$ , and so on, representing an anisotropic permeability) are available as `br.kappaxx`, `br.kappayy`, and so on (using the default name `br`).

### *Forchheimer Drag*

---

The **Forchheimer Drag** subnode is available from the context menu (right-click the **Fluid and Matrix Properties** parent node) or from the **Physics** toolbar, **Attributes** menu.

While the drag of the fluid on the porous matrix in the basic Brinkman equations is proportional to the flow velocity, (Darcy's law drag), the Forchheimer drag is proportional to the square of the fluid velocity. The latter term accounts for an inertial turbulent drag effect that comes into play for fast flows through large pores. Adding the Forchheimer term takes into account all drag contributions that the Ergun equation covers.

## FORCHHEIMER DRAG

Enter a value for the **Forchheimer coefficient**  $\beta_F$  (SI unit:  $\text{kg}/\text{m}^4$ ). The default is 0  $\text{kg}/\text{m}^4$ .

### *Mass Source*

---

The **Mass Source** node adds a mass source (or mass sink)  $Q_{br}$  to the right-hand side of the continuity equation: [Equation 5-10](#). 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.

$$\frac{\partial}{\partial t}(\epsilon_p \rho) + \nabla \cdot (\rho \mathbf{u}) = Q_{br} \quad (5-5)$$

## DOMAIN SELECTION

Only Porous Matrix domains are available.

### MASS SOURCE

Enter a value or expression for the **Source term**  $Q_{br}$  (SI unit:  $\text{kg}/(\text{m}^3 \cdot \text{s})$ ). The default is  $0 \text{ kg}/(\text{m}^3 \cdot \text{s})$ .

### *Volume Force*

---

Use the **Volume Force** node to specify the force  $\mathbf{F}$  on the right-hand side of [Equation 5-11](#). It then acts on each fluid element in the specified domains. A common application is to include gravity effects.

$$\frac{\rho}{\varepsilon_p} \left( \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \frac{\mathbf{u}}{\varepsilon_p} \right) = -\nabla p + \nabla \cdot \left[ \frac{1}{\varepsilon_p} \left\{ \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) \mathbf{I} \right\} \right] - \left( \kappa^{-1} \mu + \frac{Q_{br}}{\varepsilon_p^2} \right) \mathbf{u} + \mathbf{F} \quad (5-6)$$

### VOLUME FORCE

Enter the components of **Volume force**  $\mathbf{F}$  (SI unit:  $\text{N}/\text{m}^3$ ).

### *Initial Values*

---

The **Initial Values** node adds initial values for the velocity field and the pressure that can serve as an initial condition for a transient simulation or as an initial guess for a nonlinear solver.

### INITIAL VALUES

Enter initial values or expressions for the **Velocity field**  $\mathbf{u}$  (SI unit:  $\text{m}/\text{s}$ ) and the **Pressure**  $p$  (SI unit: Pa). The default values are  $0 \text{ m}/\text{s}$  and  $0 \text{ Pa}$ , respectively.

### *Fluid Properties*

---

The **Fluid Properties** node adds the momentum and continuity equations to solve for free flow in non-porous 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 and/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  $p_{\text{ref}}$  is from the user input defined at the physics interface level. When  $p_{\text{ref}}$  is non zero, the physics interface solves for a gauge pressure. If the pressure field instead is an absolute pressure field,  $p_{\text{ref}}$  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**  $\mu$  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.

# Theory for the Darcy's Law Interface

The [Darcy's Law Interface](#) theory is described in this section.

In a porous medium, the global transport of momentum by shear stresses in the fluid is often negligible: the pore walls impede momentum transport between fluid occupying different pores. In most applications, a detailed description of the resolution of every pore is not practical. 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 provides a complete mathematical model suitable for a variety of applications involving porous media flows when the pressure gradient is the major driving force.

## *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:

$$\mathbf{u} = -\frac{\kappa}{\mu}\nabla p \quad (5-7)$$

In this equation,  $\kappa$  (SI unit:  $\text{m}^2$ ) denotes the permeability of the porous medium,  $\mu$  (SI unit:  $\text{kg}/(\text{m}\cdot\text{s})$ ) the dynamic viscosity of the fluid,  $p$  (SI unit: Pa) the pressure, and  $\mathbf{u}$  (SI unit:  $\text{m}/\text{s}$ ) the Darcy velocity. The Darcy's Law interface combines Darcy's law with the continuity equation:

$$\frac{\partial}{\partial t}(\rho\varepsilon) + \nabla \cdot (\rho\mathbf{u}) = Q_m \quad (5-8)$$

In the above equation,  $\rho$  (SI unit:  $\text{kg}/\text{m}^3$ ) is the density of the fluid,  $\varepsilon$  (dimensionless) is the porosity, and  $Q_m$  (SI unit:  $\text{kg}/(\text{m}^3\cdot\text{s})$ ) is a mass source term. 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.

If the Darcy's Law interface is coupled to an energy balance, then the fluid density can be a function of the temperature, pressure, and composition (for mixture flows). For gas flows in porous media, the relation is given by the ideal gas law:

$$\rho = \frac{pM}{RT} \quad (5-9)$$

where  $R= 8.314 \text{ J}/(\text{mol}\cdot\text{K})$  is the universal gas constant,  $M$  (SI unit:  $\text{kg}/\text{mol}$ ) is the molecular weight of the gas, and  $T$  (SI unit:  $\text{K}$ ) is the temperature.

# 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*

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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 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:

$$\frac{\partial}{\partial t}(\epsilon_p \rho) + \nabla \cdot (\rho \mathbf{u}) = Q_{br} \quad (5-10)$$

$$\begin{aligned} \frac{\rho}{\epsilon_p} \left( \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \frac{\mathbf{u}}{\epsilon_p} \right) = \\ -\nabla p + \nabla \cdot \left[ \frac{1}{\epsilon_p} \left\{ \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) \mathbf{I} \right\} \right] - \left( \boldsymbol{\kappa}^{-1} \mu + \frac{Q_{br}}{\epsilon_p^2} \right) \mathbf{u} + \mathbf{F} \end{aligned} \quad (5-11)$$

In these equations:

- $\mu$  (SI unit: kg/(m·s)) is the dynamic viscosity of the fluid
- $\mathbf{u}$  (SI unit: m/s) is the velocity vector
- $\rho$  (SI unit: kg/m<sup>3</sup>) is the density of the fluid
- $p$  (SI unit: Pa) is the pressure
- $\epsilon_p$  is the porosity
- $\boldsymbol{\kappa}$  (SI unit: m<sup>2</sup>) is the permeability tensor of the porous medium, and
- $Q_{br}$  (SI unit: kg/(m<sup>3</sup>·s)) is a mass source or mass sink

Influence of gravity and other volume forces can be accounted for via the force term  $\mathbf{F}$  (SI unit: kg/(m<sup>2</sup>·s<sup>2</sup>)).

When the Neglect inertial term (Stokes-Brinkman) check box is selected, the term  $(\mathbf{u} \cdot \nabla)(\mathbf{u}/\epsilon_p)$  on the left-hand side of Equation 5-11 is disabled.

The mass source,  $Q_{br}$ , accounts for mass deposit and mass creation within the domains. The mass exchange is assumed to occur at zero velocity.

The Forchheimer drag option,  $\beta_F$  (SI unit: kg/m<sup>4</sup>), adds a viscous force proportional to the square of the fluid velocity,  $\mathbf{F}_F = -\beta_F |\mathbf{u}| \mathbf{u}$ , to the right-hand side of Equation 5-11.

In case of a flow with variable density, Equation 5-10 and Equation 5-11 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

$$\frac{\partial}{\partial t}(\epsilon_p \rho) + \mathbf{u} \cdot \nabla \rho = 0$$

and the continuity equation (Equation 5-10) reduces to

$$\rho \nabla \cdot \mathbf{u} = Q_{\text{br}}$$

*References for the Brinkman Equations Interface*

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1. D. Nield and A. Bejan, *Convection in Porous Media*, 3rd ed., Springer, 2006.
2. M. Le Bars and M.G. Worster, “Interfacial Conditions Between a Pure Fluid and a Porous Medium: Implications for Binary Alloy Solidification,” *J. of Fluid Mechanics*, vol. 550, pp. 149–173, 2006.

# Theory for the Coupling of Fluid Flow to Electrochemical Reactions

This section briefly discusses [Momentum Sources and Sinks](#). Also see [Theory for the Coupling of Mass Transport to Electrochemical Reactions](#) for how to calculate molar and mass fluxes, sources and sinks.

## *Momentum Sources and Sinks*

---

The flow velocity,  $\mathbf{u}$  (SI unit: m/s), at a boundary is coupled to the total mass flux of the species at the electrode surface in the following way

$$\mathbf{u} \cdot \mathbf{n} = \frac{1}{\rho} \sum_i \mathbf{n}_i \cdot \mathbf{n} \quad (5-12)$$

where  $\rho$  (SI unit: kg/m<sup>3</sup>) 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

$$\mathbf{u} = - \left( \frac{1}{\rho} \sum_i M_i N_i \right) \mathbf{n} \quad (5-13)$$

where  $M_i$  (SI unit: kg/mol) is the species mass and  $N_i$  (SI unit: mol/(m<sup>2</sup>·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:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = \sum_i R_{i, \text{mass}} \quad (5-14)$$

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.



## 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 Electrochemistry 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 Electrochemistry 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 Multiphysics nodes that become available in the model builder tree if there is both a Heat Transfer interfaces and an Electrochemistry interface available in the same component.

The [Electrochemical Heat Source](#) 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.

The [Boundary Electrochemical Heat Source](#) multiphysics node defines a boundary heat source (flux) in the heat transfer interface, based on the sum of irreversible activation losses and reversible heat in the electrochemistry interface.

The [Temperature Coupling](#) node can be used to set 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.



- [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

$$Q_{\text{JH}} = -(\mathbf{i}_s \cdot \nabla \phi_s + \mathbf{i}_l \cdot \nabla \phi_l) \quad (6-1)$$

### *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

$$Q_m = \left( \frac{\Delta H_m}{n_m F} - \left( \frac{\Delta G_m}{n_m F} - \eta_{m, \text{tot}} \right) \right) i_m \quad (6-2)$$

where  $\Delta H_m$  is the enthalpy change of the reaction, and  $\Delta G_m$  is the Gibbs free energy of the reaction,  $\Delta G_m$ , defined as

$$\Delta G_m = \Delta H_m - T \Delta S_m$$

where  $\Delta S_m$  is the net entropy change. The equilibrium potential is related to  $\Delta G_m$  in the following way:

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

In [Equation 6-2](#) we have used the total overpotential,  $\eta_{m, \text{tot}}$ , (including potential effects from film resistances and similar), defined as

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

By the relation

$$\frac{\partial E_{\text{eq},m}}{\partial T} = \frac{\Delta S_m}{n_m F}$$

the local heat source due to the electrochemical conversion process becomes

$$Q_m = \left( \eta_{m,\text{tot}} + T \frac{\partial E_{\text{eq},m}}{\partial T} \right) i_m$$

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.



# Multiphysics Coupling Nodes

The Electrochemistry 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** 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** node. When you right-click this node, you can choose from the available multiphysics couplings.



[The Multiphysics Node](#) in the *COMSOL Multiphysics Reference Manual*.


---

In this chapter, the following multiphysics couplings nodes are described:

- [Boundary Electrochemical Heat Source](#)
- [Electrochemical Heat Source](#)
- [Flow Coupling](#)
- [Potential Coupling](#)
- [Space Charge Density Coupling](#)
- [Temperature Coupling](#)

### *Boundary Electrochemical Heat Source*

---

This multiphysics coupling () defines a boundary heat source (flux) in a heat transfer interface, based on the sum of irreversible activation losses and reversible heat in the electrochemistry interface.

The settings of this node are similar to the [Electromagnetic Heat Source](#). You can also select **None** from either list to uncouple the [Electromagnetic Heat Source](#) node from a physics interface. If the physics interface is removed from the *Model Builder* (for example, *Heat Transfer in Solids* is deleted), then the *Heat transfer* list defaults to **None** as there is nothing to couple to., described in the *COMSOL Multiphysics Reference Manual*.




[Coupling of Heat Transfer to Electrochemical Reactions](#)

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### *Electrochemical Heat Source*

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Use this multiphysics coupling () to define a domain heat source in a heat transfer interface, based on the sum of irreversible (Joule heating and activation losses) and reversible heat in an electrochemistry interface.

The settings of this node are similar to the [Electromagnetic Heat Source](#), described in the *COMSOL Multiphysics Reference Manual*.




[Coupling of Heat Transfer to Electrochemical Reactions](#)

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## Flow Coupling

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This multiphysics coupling () defines  $\mathbf{u}$  and  $p$  variables in order to set the model inputs in a physics interface that defines convective transport. In addition it provides all the fluids quantities that may be needed by the interface (for example, viscosity, turbulence parameters).

### SETTINGS

The **Label** is the default multiphysics coupling feature name.

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

The default **Name** (for the first multiphysics coupling feature in the model) is `fc1`.

### FLOW COUPLING

This section defines the physics involved in the multiphysics coupling. By default, the applicable physics interface is selected in the **Source** list to apply the **Destination** to its physics interface to establish the coupling.

You can also select **None** from either list to uncouple the node from a physics interface. If the physics interface is removed from the **Model Builder** — for example, **Heat Transfer in Solids** is deleted — then the **Destination** list defaults to **None** as there is nothing to couple to.



If a physics interface is deleted and then added to the model again, and in order to re-establish the coupling, you need to choose the physics interface again from the lists. This is applicable to all multiphysics coupling nodes that would normally default to the once present physics interface. See [Multiphysics Modeling Approaches](#) in the *COMSOL Multiphysics Reference Manual*.

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## Potential Coupling

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This node applies the potential variable from the source interface into the model inputs of the destination interface.

### *Space Charge Density Coupling*

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This node 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.

### *Temperature Coupling*

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Use this multiphysics coupling to add the temperature as the default model input for a standalone physics interface.

The **Temperature Coupling** feature is generic and specifies a Heat Transfer interface as **Source** and a second interface as **Destination**. When **Temperature Coupling** feature is used, the temperature from the **Source** is used to evaluate material properties in any feature from the **Destination** interface. The coupling can be added wherever the Heat Transfer interface is active.

The **Source** interface can be any interface defining a temperature, which includes all versions of heat transfer and multiphysics, except the pure radiation interfaces.

The **Destination** interface can be any interface providing multiphysics feature in the **Multiphysics** node — for example, **Electric Current** or **Solid Mechanics**.

See [Temperature Coupling](#) in the *COMSOL Multiphysics Reference Manual* for more details about this multiphysics coupling.

## Glossary

This [Glossary of Terms](#) contains application-specific terms used in the Electrochemistry 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  $\phi_s$  (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  $\phi_l$  (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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