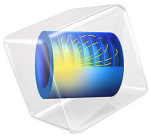


Model created in COMSOL Multiphysics 6.4

# Current Distribution in a Chlor–Alkali Membrane Cell

## *Introduction*

The chlor-alkali membrane process is one of the largest processes in industrial electrolysis with production of roughly 40 million metric tons of both chlorine and caustic soda per year (Ref. 1). Chlorine's largest use is in the production of vinyl chloride monomer, which in turn is used for the production of polyvinyl chloride (PVC). Among the applications of PVC are as electrical insulator in cables and as a material for pipes, carpets, raincoats, and many other products. The production of chlorine implies a simultaneous production of caustic soda (alkali), which is widely used in the chemical industry for alkalization and neutralization of acidic streams. Caustic soda is also used in alkaline batteries.

The traditional process for manufacturing chlorine and caustic soda is the mercury-cell process. This technology has been partly replaced by the diaphragm process, and in later years the membrane process has been the dominating process in retrofits and for new plants. The purpose of the diaphragm or membrane is to separate the products chlorine and caustic soda, which otherwise would react to produce hypochlorite and hydrochloric acid. Chlorine and caustic soda are produced at the anode and cathode, respectively. Figure 1 shows a diagram of the process.

Current density in membrane-cell technology has increased dramatically during the last decade as the membranes themselves have improved. This results in lower investment costs for greater production. However, the increase in current density implies an increase in power consumption if nothing is done to dampen the voltage increase. Advances in cell design by increased internal convection, decreased ohmic losses, and better membranes have allowed for large increases in current density with small increases in cell voltage. One of the important parameters in the design of modern membrane cells is the current-density distribution on the electrode surfaces. It is important, from the viewpoint of catalyst lifetime and minimization of losses, that the current density on the electrode frontal surfaces is as uniform as possible.

This example describes the current-density distribution in a realistic structure for the anodes and cathodes in a membrane cell. This discussion limits the model to one unit cell of the entire cell. This unit cell appears on the right side in Figure 1.

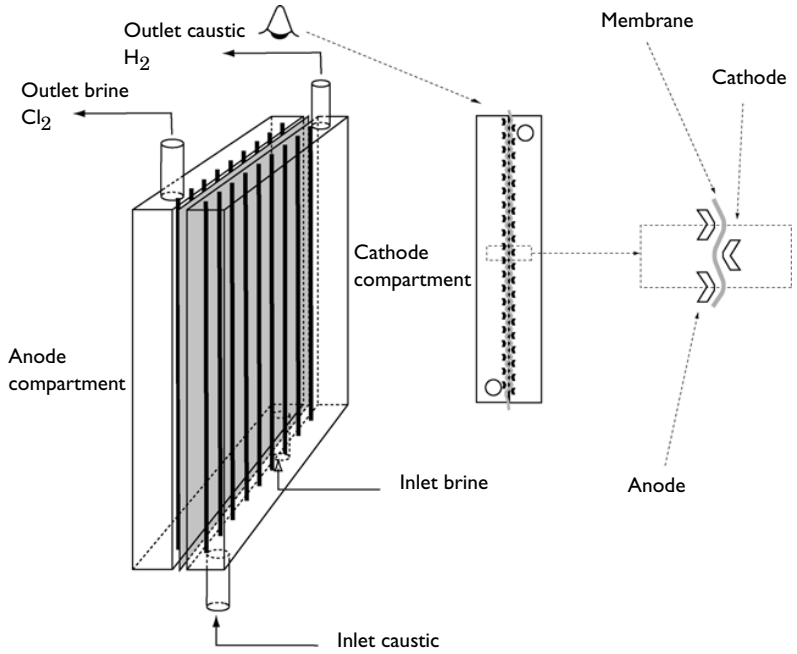



*Figure 1: Drawing of the unit cell.*

The anode and cathode ribs are separated by the membrane, which is a cation-selective membrane. It is forced to adapt its shape to fit within the interelectrode distance. The membrane prevents mixing between brine and chlorine on the anode side with the caustic soda and hydrogen on the cathode side.

A detailed description of the process of chlor-alkali electrolysis is available in Ref. 1.

## *Model Definition*

This example models the current and potential distribution in a unit cell in the membrane cell sketched in Figure 1. This model is a secondary current-distribution model (see Ref. 2), which implies that the dependence of the electron transfer on the local potential is taken into account, and that constant composition in the subdomains is assumed. The electron transfer reactions at the anode and cathode surfaces are:

$$2Cl^- \Leftrightarrow Cl_2(g) + 2e^- \qquad \text{at the anode}$$

$$2H_2O + 2e^- \Leftrightarrow H_2(g) + 2OH^- \quad \text{at the cathode}$$

The domain in the model is half of the unit cell shown in Figure 1, as explained in Figure 2.

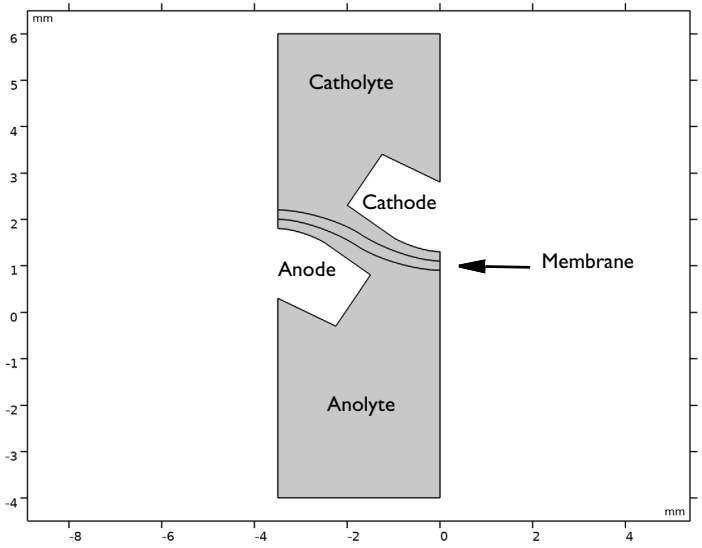



*Figure 2: Model geometry.*

The chemical reactions show that there is gas evolution in both the anodic and cathodic compartments, creating a vigorous internal convection in the respective compartments. This makes it possible to simplify the model by neglecting the concentration gradients in the anolyte and catholyte. The simplification implies that the transport of ionic current inside the cell takes place exclusively through migration, that is, the electric field induces a flux of ions. For this reason you do not need to model the complex problem of internal free convection of the two-phase flow in order to get an estimation of the current-density distribution in the cell (see also the theory for the Current Distribution interfaces in the *Electrochemistry Module User's Guide*).

The current conduction in the membrane and two electrolyte chambers is modeled by using the Secondary Current Distribution interface, with different values for the electrolyte conductivity in each domain.

The anode reaction is very fast, and small changes in the potential result in large changes in the current density. This implies that an overpotential (primary condition) at the anode's surface is negligible:

$$E_{\mathrm{eq,a}} = \phi_{\mathrm{s,a}} - \phi_{\mathrm{l,a}} \tag{1}$$

Here $E_{\mathrm{eq,a}}$ is the equilibrium potential at the anode, $\phi_{\mathrm{s,a}}$ is the solid phase potential, and $\phi_{\mathrm{l,a}}$ is the electrolyte potential at the anode side. In this case this gives an error in potential of approximately 20 mV at that surface (Ref. 3).

The cell voltage, $E_{\mathrm{cell}}$, can be written as the difference in metal potential between the anode and cathode:

$$E_{\mathrm{cell}} = \phi_{\mathrm{s,a}} - \phi_{\mathrm{s,c}} \tag{2}$$

The cell potential may also be expressed based on the equilibrium potentials and the cell polarization potential as:

$$E_{\mathrm{cell}} = E_{\mathrm{eq,a}} - E_{\mathrm{eq,c}} + E_{\mathrm{pol}} \tag{3}$$

which results in

$$\phi_{\mathrm{s,c}} = \phi_{\mathrm{s,a}} - (E_{\mathrm{eq,a}} - E_{\mathrm{eq,c}} + E_{\mathrm{pol}}) \tag{4}$$

Grounding the electrolyte potential at the anode, $\phi_{\mathrm{l,a}}$, gives

$$\phi_{\mathrm{l,a}} = 0 \tag{5}$$

which is used as a boundary condition for the anode boundary.

In combination with the primary condition above this results in

$$\phi_{\mathrm{s,c}} = -(-E_{\mathrm{eq,c}} + E_{\mathrm{pol}}) \tag{6}$$

Using the cathode as reference potential ($E_{\mathrm{eq,c}} = 0$) when defining the kinetics this results in

$$\phi_{\mathrm{s,c}} = -E_{\mathrm{pol}} \tag{7}$$

This potential is used when defining the Butler–Volmer expression for the relation between current density and potential on the cathode electrode boundary.

Figure 3 shows the potential in the anode and cathode compartments as well as in the membrane electrolyte. From this plot note that the largest ohmic losses arise in the membrane, as expected from its low conductivity.

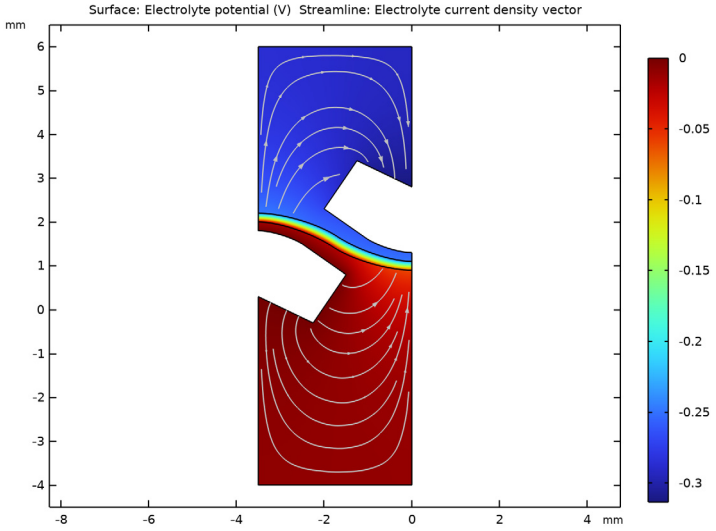



*Figure 3: Electrolyte potential.*

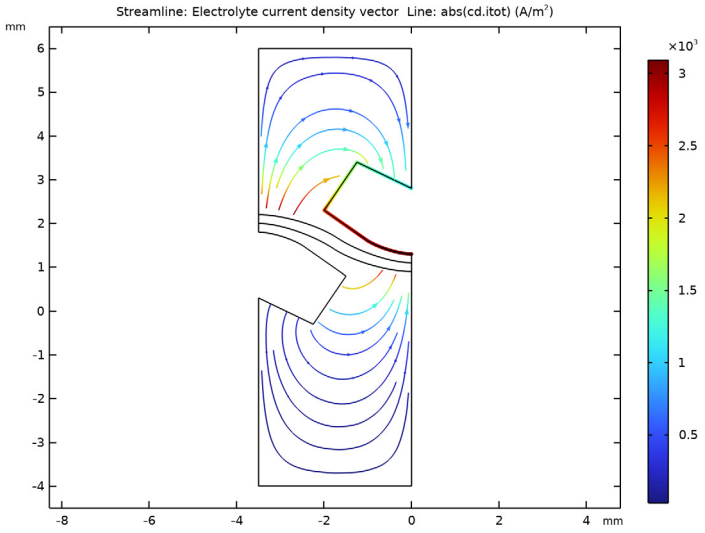



*Figure 4: Electrolyte current density magnitude.*

Figure 4 shows the electrolyte current streamlines, with the color indicating modulus of the current-density vector. This plot hence illustrates "hot spots" in the electrolyte where the current density is large. On the parts of the electrodes where the current density is high, catalyst can be lost due to accelerated wear.

## *References*

1. H.S. Burney, "Past Present and Future of the Chlor-Alkali Industry," *Chlor-Alkali and Chlorate Technology: R.B. Macmullin Memorial Symposium*, *Proc Electrochemical Society,* vol. 99–21, 1999.

2. J.S. Newman, *Electrochemical Systems*, 2nd ed., Prentice Hall, 1991.

3. P. Bosander, P. Byrne, E. Fontes, and O. Parhammar, "Current Distribution on a Membrane Cell Anode," *Chlor-Alkali and Chlorate Technology: R.B. Macmullin Memorial Symposium*, *Proc Electrochemical Society,* vol. 99–21, 1999.

**Application Library path:** `Electrochemistry_Module/Electrochemical_Engineering/chlor_alkali`

## *Modeling Instructions*

From the **File** menu, choose **New**.

### NEW

In the **New** window, click **Model Wizard**.

### MODEL WIZARD

1 In the **Model Wizard** window, click **2D**.

2 In the **Select Physics** tree, select **Electrochemistry** > **Primary and Secondary Current Distribution** > **Secondary Current Distribution (cd)**.

3 Click **Add**.

4 Click **Study**.

5 In the **Select Study** tree, select **General Studies** > **Stationary**.

6 Click **Done**.

### GLOBAL DEFINITIONS

Start by loading the model parameters from a text file.

*Parameters 1*

1 In the **Model Builder** window, under **Global Definitions** click **Parameters 1**.

2 In the **Settings** window for **Parameters**, locate the **Parameters** section.

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `chlor_alkali_parameters.txt`.

### GEOMETRY 1

The model geometry is available as a parameterized geometry sequence in a separate MPH file. If you want to build it from scratch, follow the instructions in the section Appendix — Geometry Modeling Instructions. Otherwise load it from file with the following steps.

1 In the **Geometry** toolbar, click **Insert Sequence** and choose **Insert Sequence**.

2 Browse to the model's Application Libraries folder and double-click the file `chlor_alkali_geom_sequence.mph`.

3 In the **Geometry** toolbar, click **Build All**.

4 Click the **Zoom Extents** button in the **Graphics** toolbar.

### MATERIALS

Define the electrolyte conductivity in the three different domains by adding separate materials for the catholyte, the membrane and the anolyte.

*Material 1 (mat1)*

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Materials** and choose **Blank Material**.

2 In the **Settings** window for **Material**, locate the **Geometric Entity Selection** section.

3 Click **Clear Selection**.

4 Select Domain 3 only.

5 Locate the **Material Contents** section. In the table, enter the following settings:

| Property | Variable | Value | Unit | Property group |
|---|---|---|---|---|
| Electrolyte conductivity | sigmal_iso ; sigmalii = sigmal_iso, sigmalij = 0 | K_c | S/m | Electrolyte conductivity |

*Material 2 (mat2)*

1 Right-click **Materials** and choose **Blank Material**.

2 Select Domain 2 only.

3 In the **Settings** window for **Material**, locate the **Material Contents** section.

4 In the table, enter the following settings:

| Property | Variable | Value | Unit | Property group |
|---|---|---|---|---|
| Electrolyte conductivity | sigmal_iso ; sigmalii = sigmal_iso, sigmalij = 0 | K_m | S/m | Electrolyte conductivity |

*Material 3 (mat3)*

1 Right-click **Materials** and choose **Blank Material**.

2 Select Domain 1 only.

3 In the **Settings** window for **Material**, locate the **Material Contents** section.

4 In the table, enter the following settings:

| Property | Variable | Value | Unit | Property group |
|---|---|---|---|---|
| Electrolyte conductivity | sigmal_iso ; sigmalii = sigmal_iso, sigmalij = 0 | K_a | S/m | Electrolyte conductivity |

### SECONDARY CURRENT DISTRIBUTION (CD)

Set up the cathode current density by using an Electrode Surface node. Define the exchange current density in the Electrode Reaction child node.

*Electrode Surface 1*

1 In the **Physics** toolbar, click **Boundaries** and choose **Electrode Surface**.

2 Select Boundaries 10–12 and 22 only.

3 In the **Settings** window for **Electrode Surface**, locate the **Electrode Phase Potential Condition** section.

4 In the $\phi_{s,ext}$ text field, type `-E_pol`.

*Electrode Reaction 1*

1 In the **Model Builder** window, click **Electrode Reaction 1**.

2 In the **Settings** window for **Electrode Reaction**, locate the **Electrode Kinetics** section.

3 From the **Kinetics expression type** list, choose **Butler–Volmer**.

4 In the $i_0$ text field, type `i0_c`.

*Electrolyte Potential 1*

Assuming fast reaction kinetics, a constant potential is set at the anode surface.

Define the potential on the anode by using an Electrolyte Potential node.

1 In the **Physics** toolbar, click **Boundaries** and choose **Electrolyte Potential**.

2 Select Boundaries 3, 8, 9, and 17 only.

### GLOBAL DEFINITIONS

*Default Model Inputs*

Set up the temperature value used in the entire model.

1 In the **Model Builder** window, under **Global Definitions** click **Default Model Inputs**.

2 In the **Settings** window for **Default Model Inputs**, locate the **Browse Model Inputs** section.

3 In the tree, select **General** > **Temperature (K) - minput.T**.

4 Find the **Expression for remaining selection** subsection. In the **Temperature** text field, type T.

### MESH 1

Create a triangular mesh with a higher resolution at the electrode surfaces and on the membrane boundaries.

*Free Triangular 1*

In the **Mesh** toolbar, click  **Free Triangular**.

*Size 1*

1 Right-click **Free Triangular 1** and choose **Size**.

2 In the **Settings** window for **Size**, locate the **Geometric Entity Selection** section.

3 From the **Geometric entity level** list, choose **Boundary**.

Select the anode, cathode and membrane boundaries. The easiest way to do this is by using a selection box around the central part of the geometry.

4 Select Boundaries 3–5, 8–12, 14, 15, and 17–22 only.

5 Locate the **Element Size** section. From the **Predefined** list, choose **Extremely fine**.

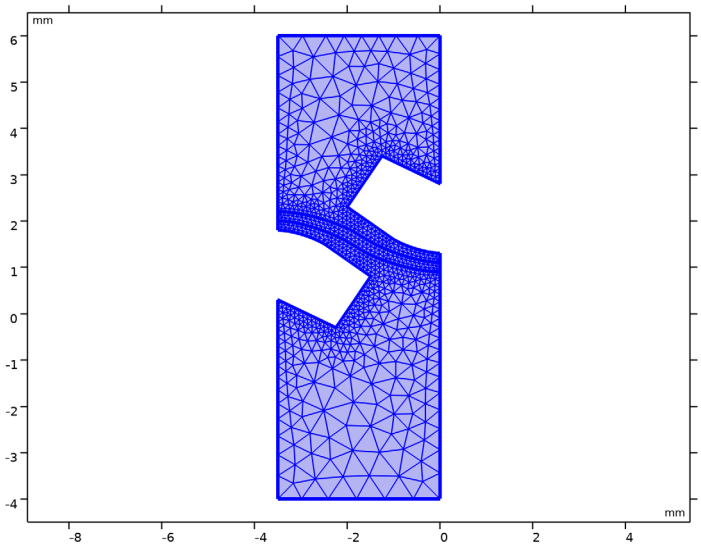
6 In the **Model Builder** window, right-click **Mesh 1** and choose **Build All**.

*Free Triangular 1*

1 In the **Model Builder** window, right-click **Free Triangular 1** and choose **Build All**.

2 Click the **Zoom Extents** button in the **Graphics** toolbar.

The finalized mesh should now look like this:




## STUDY 1

The problem is now ready for solving.

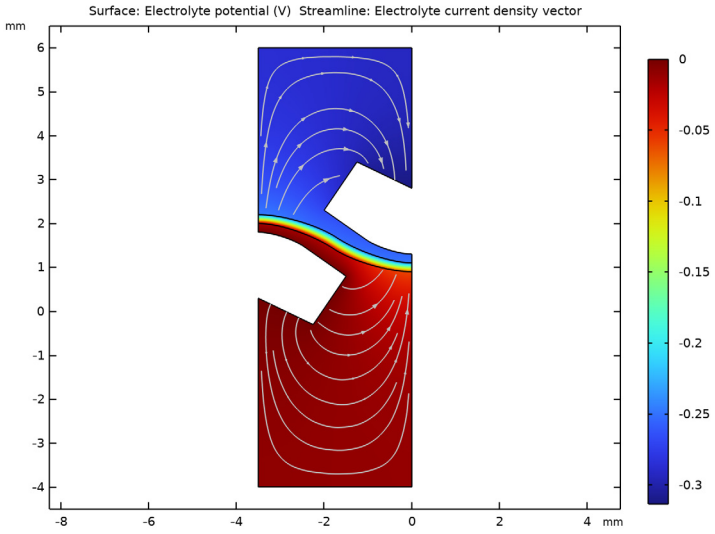
1 In the **Study** toolbar, click **Compute**.

## RESULTS

### *Electrolyte Potential (cd)*

The first default plot shows the electrolyte potential and an arrow plot of the electrolyte currents.

1 Click the **Zoom Extents** button in the **Graphics** toolbar.

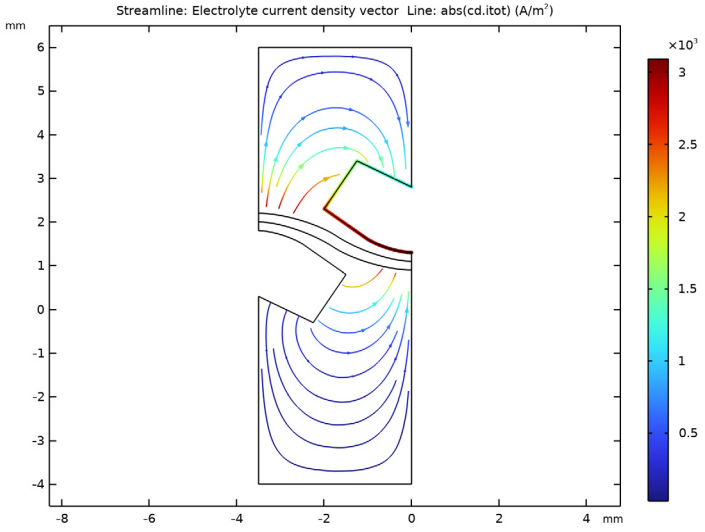



### *Electrolyte Current Density (cd)*

The second default plot visualizes the electrolyte current density.

1 In the **Model Builder** window, click **Electrolyte Current Density (cd)**.

2 In the **Electrolyte Current Density (cd)** toolbar, click **Plot**.



From the **File** menu, choose **New**.

### NEW

In the **New** window, click **Blank Model**.

### ADD COMPONENT

In the **Home** toolbar, click **Add Component** and choose **2D**.

### GEOMETRY 1

1 In the **Settings** window for **Geometry**, locate the **Units** section.

2 From the **Length unit** list, choose **mm**.

*Rectangle 1 (r1)*

1 In the **Geometry** toolbar, click **Rectangle**.

2 In the **Settings** window for **Rectangle**, locate the **Size and Shape** section.

3 In the **Width** text field, type `3.5`.

4 In the **Height** text field, type `10`.

5 Locate the **Position** section. In the **x** text field, type `-3.5`.

6 In the **y** text field, type `-4`.

*Quadratic Bézier 1 (qb1)*

1 In the **Geometry** toolbar, click **More Primitives** and choose **Quadratic Bézier**.

2 In the **Settings** window for **Quadratic Bézier**, locate the **Control Points** section.

3 In row **1**, set **x** to `-2.5`.

4 In row **1**, set **y** to `1.5`.

5 In row **2**, set **x** to `-3`.

6 In row **2**, set **y** to `1.8`.

7 In row **3**, set **x** to `-3.5`.

8 In row **3**, set **y** to `1.8`.

*Polygon 1 (pol1)*

1 In the **Geometry** toolbar, click **Polygon**.

2 In the **Settings** window for **Polygon**, locate the **Object Type** section.

3 From the **Type** list, choose **Open curve**.

4 Locate the **Coordinates** section. From the **Data source** list, choose **Vectors**.

5 In the **x** text field, type `-3.5 -3.5 -3.5 -2.25 -2.25 -1.5 -1.5 -2.5`.

6 In the **y** text field, type `1.8 0.3 0.3 -0.3 -0.3 0.8 0.8 1.5`.

*Convert to Solid 1 (csol1)*

1 In the **Geometry** toolbar, click  **Conversions** and choose **Convert to Solid**.

2 Select the objects **pol1** and **qb1** only.

*Quadratic Bézier 2 (qb2)*

1 In the **Geometry** toolbar, click  **More Primitives** and choose **Quadratic Bézier**.

2 In the **Settings** window for **Quadratic Bézier**, locate the **Control Points** section.

3 In row **1**, set **x** to `-1.75`.

4 In row **1**, set **y** to `1.7`.

5 In row **2**, set **x** to `-2.55`.

6 In row **2**, set **y** to `2.2`.

7 In row **3**, set **x** to `-3.5`.

8 In row **3**, set **y** to `2.2`.

*Line Segment 1 (ls1)*

1 In the **Geometry** toolbar, click  **More Primitives** and choose **Line Segment**.

2 In the **Settings** window for **Line Segment**, locate the **Starting Point** section.

3 From the **Specify** list, choose **Coordinates**.

4 Locate the **Endpoint** section. From the **Specify** list, choose **Coordinates**.

5 Locate the **Starting Point** section. In the **x** text field, type `-3.5`.

6 In the **y** text field, type `2.2`.

7 Locate the **Endpoint** section. In the **x** text field, type `-3.5`.

8 In the **y** text field, type `2`.

*Quadratic Bézier 3 (qb3)*

1 In the **Geometry** toolbar, click  **More Primitives** and choose **Quadratic Bézier**.

2 In the **Settings** window for **Quadratic Bézier**, locate the **Control Points** section.

3 In row **1**, set **x** to `-3.5`.

4 In row **1**, set **y** to `2`.

5 In row **2**, set **x** to `-2.63`.

6 In row **2**, set **y** to 2.

7 In row **3**, set **x** to -1.75.

8 In row **3**, set **y** to 1.4.

*Line Segment 2 (ls2)*

1 In the **Geometry** toolbar, click **More Primitives** and choose **Line Segment**.

2 In the **Settings** window for **Line Segment**, locate the **Starting Point** section.

3 From the **Specify** list, choose **Coordinates**.

4 Locate the **Endpoint** section. From the **Specify** list, choose **Coordinates**.

5 Locate the **Starting Point** section. In the **x** text field, type -1.75.

6 In the **y** text field, type 1.4.

7 Locate the **Endpoint** section. In the **x** text field, type -1.75.

8 In the **y** text field, type 1.7.

*Convert to Solid 2 (csol2)*

1 In the **Geometry** toolbar, click **Conversions** and choose **Convert to Solid**.

2 Select the objects **ls1**, **ls2**, **qb2**, and **qb3** only.

*Rotate 1 (rot1)*

1 In the **Geometry** toolbar, click **Transforms** and choose **Rotate**.

2 Select the objects **csol1** and **csol2** only.

3 In the **Settings** window for **Rotate**, locate the **Input** section.

4 Select the **Keep input objects** checkbox.

5 Locate the **Rotation** section. In the **Angle** text field, type 180.

6 Locate the **Center of Rotation** section. In the **x** text field, type -1.75.

7 In the **y** text field, type 1.55.

*Union 1 (uni1)*

1 In the **Geometry** toolbar, click **Booleans and Partitions** and choose **Union**.

2 Select the objects **csol2** and **rot1(2)** only.

3 In the **Settings** window for **Union**, locate the **Union** section.

4 Clear the **Keep interior boundaries** checkbox.

*Difference 1 (dif1)*

1 In the **Geometry** toolbar, click **Booleans and Partitions** and choose **Difference**.

2 Select the object **r1** only.

3 In the **Settings** window for **Difference**, locate the **Difference** section.

4 Click to select the **Activate Selection** toggle button for **Objects to subtract**.

5 Select the objects **csol1** and **rot1(1)** only.