

# Transport and Adsorption

## *Introduction*

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This example demonstrates how you can model phenomena defined in different dimensions (2D and 1D in this example) in a fully coupled manner using COMSOL Multiphysics.

In this particular case, the model involves a small parallel-plate reactor with a catalytic surface. Similar applications where surface processes are of critical importance include biochip devices and a semiconductor components.

When modeling chemical reactions the reaction rates are commonly functions of the concentrations of the reactants in the phase that transports the chemicals. However, for surface reactions it is also necessary to account for the surface concentrations of the active sites and surface adsorbed species. The mass balances in the bulk of the reactor must therefore be coupled to the mass balances for species, present only at the surface of the device.

## *Model Definition*

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The first approximation you can make is to reduce the 3D geometry to 2D, which is reasonable if the variations in concentration are small along the depth of the domain. [Figure 1](#) shows how the 2D model domain is related to the full 3D reactor geometry.

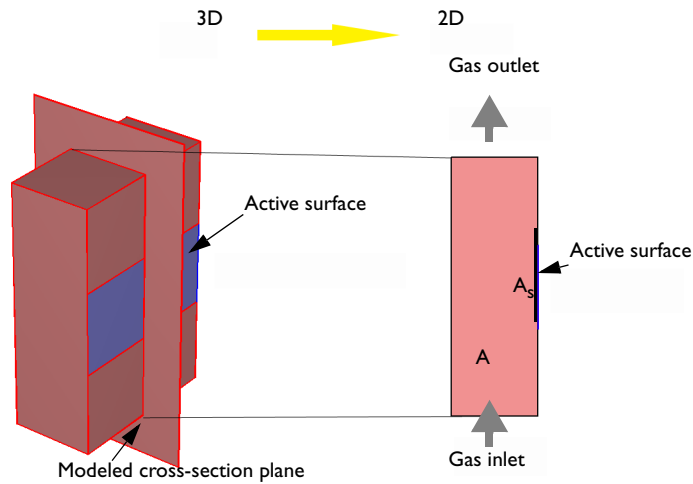
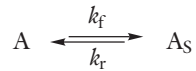


Figure 1: The modeled domain is a parallel plate reactor with an active surface where you want to model the concentration of surface species.  $A$  denotes molecular species dissolved in gas and  $A_s$  the same species adsorbed on the surface.

### MODEL EQUATIONS

The adsorption/desorption reaction at the surface is described by



where  $k_f$  and  $k_r$  are forward and reverse rate constants.  $A$  and  $A_s$  are the molecular species in the gas and adsorbed on active sites on the surface, respectively.

Let  $\theta$  be the fraction of active sites occupied by adsorbed molecules. The fraction of free sites is then  $1 - \theta$ . Langmuir derived that the rate of desorption of molecules,  $r_{\text{des}}$  ( $\text{mol}/(\text{m}^2 \cdot \text{s})$ ), is proportional to  $\theta$  and equal to  $k_r \theta$  where  $k_r$  is a constant at constant temperature. Furthermore, the rate of adsorption of molecules is proportional to both the fraction of free surface sites,  $1 - \theta$ , and to the rate of which molecules strike the surface. The collision rate is in turn directly proportional the partial pressure of the species,  $p_A$  (Pa). The rate of adsorption in  $\text{mol}/(\text{m}^2 \cdot \text{s})$  is thus  $r_{\text{ads}} = k_f p_A (1 - \theta)$ , where  $k_f$  is a constant at constant temperature.

To set up transport and reaction equations in terms of  $c$  (bulk gas concentration of A in mol/m<sup>3</sup>) and  $c_s$  (surface concentration of A in mol/m<sup>2</sup>), make the following substitutions:

$$\begin{aligned}\theta &= c_s/\Gamma_s \\ p_A &= cRT\end{aligned}$$

where

- $\Gamma_s$  is the total surface concentration of active sites (mol/m<sup>2</sup>)
- $R$  is the gas constant (J/(mol·K))
- $T$  is temperature (K)

which yields

$$r_{\text{des}} = k_{\text{des}}c_s \quad (1)$$

and

$$r_{\text{ads}} = k_{\text{ads}}c(\Gamma_s - c_s)$$

where

- $k_{\text{des}} = k_r/\Gamma_s$  is the rate constant for the desorption reaction (m<sup>3</sup>/(mol·s))
- $k_{\text{ads}} = k_pRT/\Gamma_s$  is the rate constant for the adsorption reaction (1/s)

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**Note:** The surface concentration is in moles per unit surface.

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The material balance for the surface, including surface diffusion and the reaction rate expression for the formation of the adsorbed species,  $c_s$ , is:

$$\frac{\partial c_s}{\partial t} + \nabla \cdot (-D_s \nabla c_s) = r_{\text{ads}} - r_{\text{des}}$$

where  $D_s$  represents surface diffusivity. This gives the following equation for the transport and reaction on the surface:

$$\frac{\partial c_s}{\partial t} + \nabla \cdot (-D_s \nabla c_s) = k_{\text{ads}}c(\Gamma_s - c_s) - k_{\text{des}}c_s \quad (2)$$

Equation 2 defines the units of the rate constants  $k_{\text{ads}}$  and  $k_{\text{des}}$ . The initial condition is that the concentration of adsorbed species is zero at the beginning of the process:

$$c_s = 0$$

The equation for the surface-reaction expression includes the concentration of the bulk species,  $c$ , at the position of the catalyst surface. Thus you must solve the equation for the surface reaction in combination with the mass balance in the bulk. The coupling between the mass balance in the bulk and the surface is obtained as a boundary condition in the bulk's mass balance. This condition sets the flux of  $c$  at the boundary equal to the rate of the surface reaction and is presented below. The transport in the bulk of the reactor is described by a convection-diffusion equation:

$$\frac{\partial c}{\partial t} + \nabla \cdot (-D\nabla c + c\mathbf{u}) = 0 \quad (3)$$

The initial condition sets the concentration in the bulk at  $t = 0$ :

$$c = c_0$$

In the above equation,  $D$  denotes the diffusivity of the reacting species,  $c$  is its concentration, and  $\mathbf{u}$  is the velocity. In this case, the velocity in the  $x$  direction equals 0 while the velocity in the  $y$  direction comes from the analytical expression for fully developed laminar flow between two parallel plates:

$$\mathbf{u} = (0, v_{\max} \left[ 1 - \left( \frac{x - 0.5\delta}{0.5\delta} \right)^2 \right])$$

Here,  $\delta$  is the distance between the plates,  $v_{\max}$  is the maximum local velocity, and  $x = 0$  at the left boundary of the 2D model geometry shown on the right in Figure 1.

#### BOUNDARY CONDITIONS

The boundary conditions for the surface species are insulating conditions according to:

$$\mathbf{n} \cdot (-D_s \nabla c_s) = 0 \quad (4)$$

For the bulk, the boundary condition at the active surface couples the rate of the reaction at the surface with the flux of the reacting species and the concentration of the adsorbed species and bulk species:

$$\mathbf{n} \cdot (-D\nabla c + c\mathbf{u}) = -k_{\text{ads}}c(\Gamma_s - c_s) + k_{\text{des}}c_s \quad (5)$$

The other boundary conditions for the bulk problem are:

- Inlet:  $c = c_0$
- Outlet:  $\mathbf{n} \cdot (-D\nabla c + c\mathbf{u}) = \mathbf{n} \cdot c\mathbf{u}$
- Insulation:  $\mathbf{n} \cdot (-D\nabla c + c\mathbf{u}) = 0$

### *Notes About the COMSOL Implementation*

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This example deals with a phenomenon (convection-diffusion) occurring in a 2D domain coupled to another phenomenon (diffusion-reaction) occurring only on a part of this domain's 1D boundary. Model the 2D equation (Equation 3) using a Transport of Diluted Species interface and the 1D equation (Equation 2) with a General Form Boundary PDE interface on the active-surface boundary. The two interfaces are coupled through the surface reaction rate expression on the right-hand side of Equation 2, which becomes a flux in the boundary condition Equation 5 for Equation 3. The Neumann condition Equation 4 is a natural boundary condition, which means that you do not need to impose it explicitly.

### *Results and Discussion*

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The plot in Figure 2 shows the concentration,  $c$ , of the reacting species in the 2D domain after 2 seconds of operation. The reaction is very fast and has almost reached steady state in that time frame. Figure 3, which displays the concentration along a vertical cross section of the active surface, shows that the concentration distribution exhibits edge effects at both ends of the catalyst. The higher concentration near  $y = 0$  is easy to explain because this is the position closest to the inlet, and this end is therefore continuously supplied with fresh reactant. The increase in concentration at the end closer to the outlet is due to diffusion; the edge of the surface can receive diffusion in all directions within a  $90^\circ$  angle without having to compete for the reactant supply with other parts of the catalysts. This effect also appears at the edge close to the inlet.

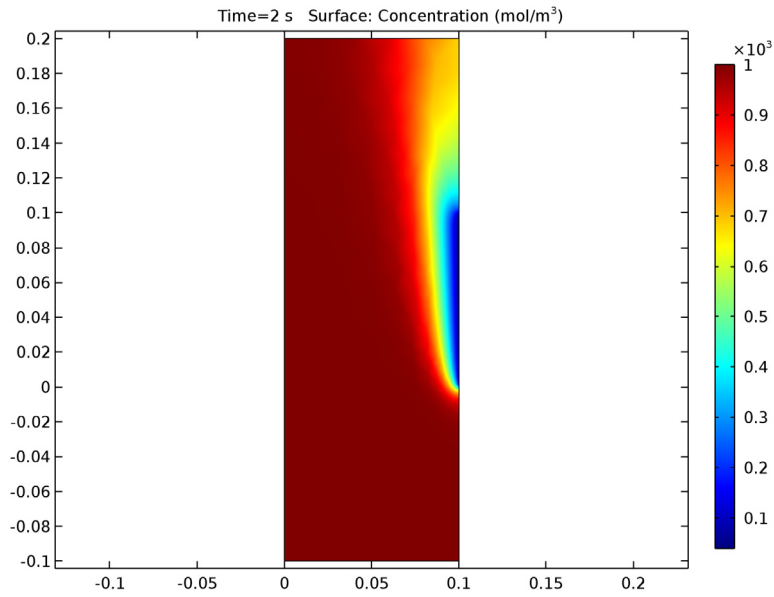


Figure 2: Concentration of the reacting species,  $c$ , after 2 seconds of operation ( $t = 2$  s).

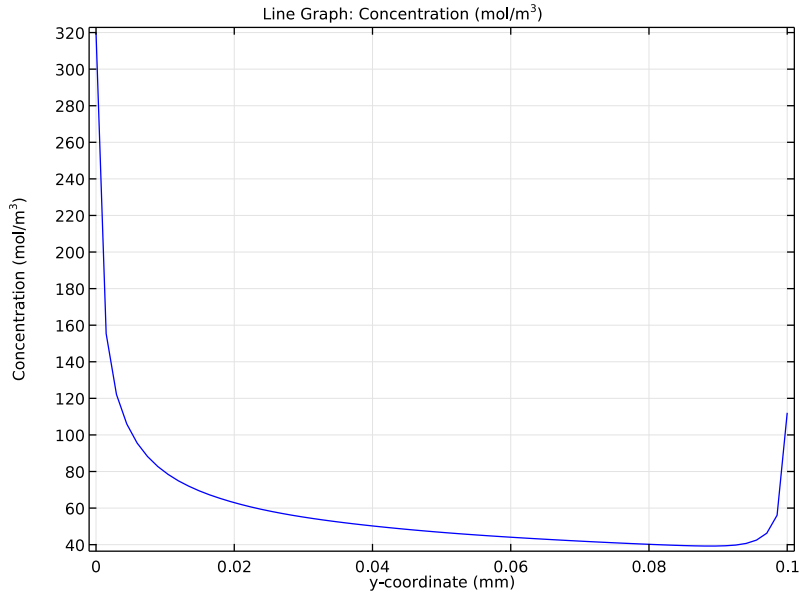
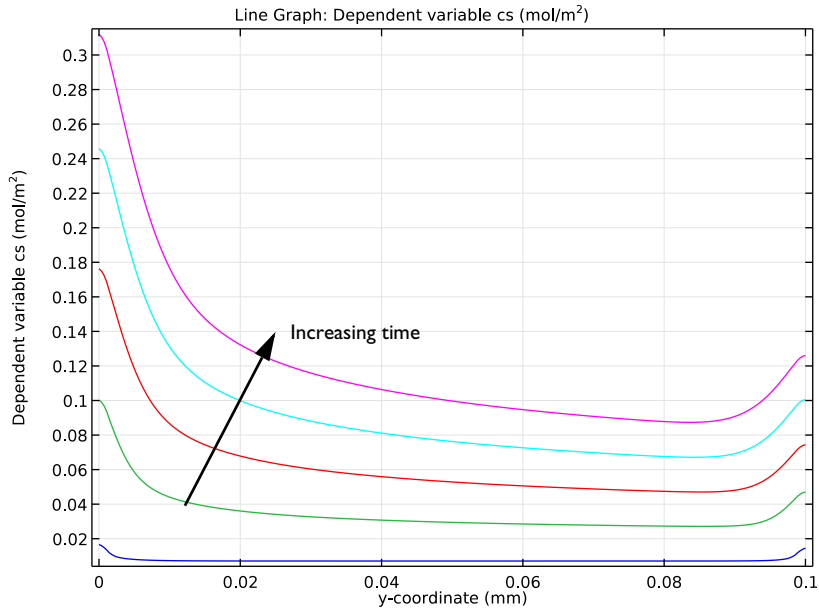


Figure 3: Concentration of the reacting species along the active surface at  $t = 2$  s.

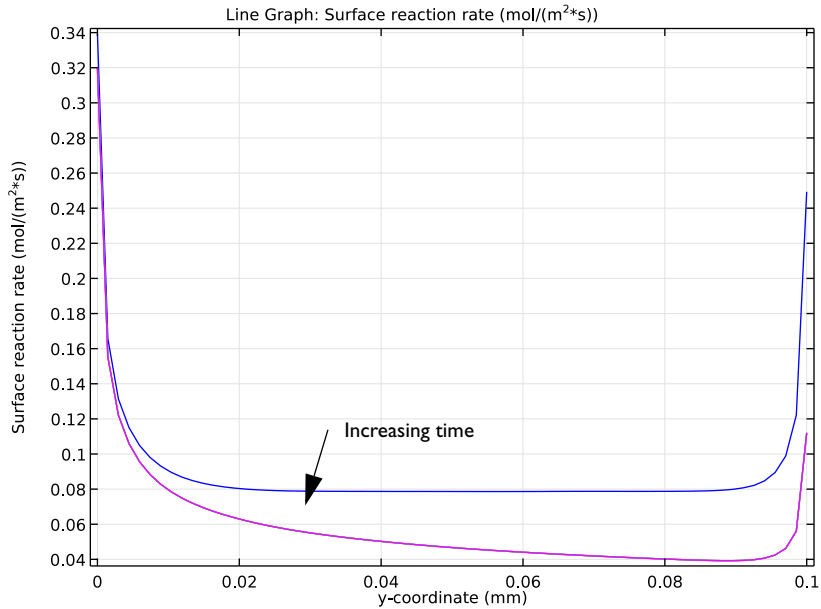
The concentration of adsorbed species,  $c_s$ , shows a similar spatial distribution. However, while the concentration of the reactant decreases with time, the concentration of adsorbed species increases. You can also see that the slight spatial diffusion evens out the concentration gradients somewhat; see [Figure 4](#).



*Figure 4: The concentration of adsorbed species increases with time. The edge effect appears at both edges due to the increased supply of reactants. This figure displays the concentration after 0.05, 0.5, 1.0, 1.5, and 2.0 s.*

The concentration of gas phase species at the surface decreases while the surface concentration of the adsorbed species increases with time. This implies that the adsorption rate decreases with time. You can see this effect in [Figure 5](#), which also shows that after 0.5 s the reaction rate almost reaches steady-state. The upper curve

shows the reaction rate after 0.05 s, while the lower curve represents the curves for 0.5, 1.0, 1.5, and 2.0 s, which are all on top of each other.



*Figure 5: Surface reaction rate at the active surface. The largest reaction rate is obtained initially and is at the edges of the active surface. The reaction process almost reaches steady state at 0.5 s.*

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**Application Library path:** COMSOL\_Multiphysics/Chemical\_Engineering/transport\_and\_adsorption

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### *Modeling Instructions*

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

#### **NEW**

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

#### **MODEL WIZARD**

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



- 2 In the **Select physics** tree, select **Chemical Species Transport>Transport of Diluted Species (tds)**.
- 3 Click **Add**.
- 4 In the **Select physics** tree, select **Mathematics>PDE Interfaces>Lower Dimensions>General Form Boundary PDE (gb)**.
- 5 Click **Add**.
- 6 In the **Dependent variables** table, enter the following settings:  

CS
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- 7 Click **Study**.
- 8 In the **Select study** tree, select **Preset Studies for Selected Physics Interfaces>Time Dependent**.
- 9 Click **Done**.

#### GLOBAL DEFINITIONS

A set of model parameters is available in a text file.

##### *Parameters*

- 1 On the **Home** toolbar, click **Parameters**.
- 2 In the **Settings** window for Parameters, locate the **Parameters** section.
- 3 Click **Load from File**.
- 4 Browse to the application's Application Library folder and double-click the file `transport_and_adsorption_parameters.txt`.

#### GEOMETRY 1

- 1 In the **Model Builder** window, under **Component 1 (comp1)** click **Geometry 1**.
- 2 In the **Settings** window for Geometry, locate the **Units** section.
- 3 From the **Length unit** list, choose **mm**.

##### *Rectangle 1 (r1)*

- 1 On the **Geometry** toolbar, click **Primitives** and choose **Rectangle**.
- 2 In the **Settings** window for Rectangle, locate the **Size** section.
- 3 In the **Width** text field, type 0.1.
- 4 In the **Height** text field, type 0.3.
- 5 Locate the **Position** section. In the **y** text field, type -0.1.

6 Click the **Build All Objects** button.

*Point 1 (pt1)*

- 1 On the **Geometry** toolbar, click **Primitives** and choose **Point**.
- 2 In the **Settings** window for Point, locate the **Point** section.
- 3 In the **x** text field, type 0.1.
- 4 Click the **Build All Objects** button.

*Point 2 (pt2)*

- 1 On the **Geometry** toolbar, click **Primitives** and choose **Point**.
- 2 In the **Settings** window for Point, locate the **Point** section.
- 3 In the **x** text field, type 0.1.
- 4 In the **y** text field, type 0.1.
- 5 Click the **Build All Objects** button.
- 6 Click the **Zoom Extents** button on the **Graphics** toolbar.

## DEFINITIONS

*Variables 1*

- 1 On the **Home** toolbar, click **Variables** and choose **Local Variables**.
- 2 In the **Settings** window for Variables, locate the **Geometric Entity Selection** section.
- 3 From the **Geometric entity level** list, choose **Boundary**.
- 4 Select Boundary 5 only.
- 5 Locate the **Variables** section. In the table, enter the following settings:

Name	Expression	Unit	Description
R	$k_{ads} \cdot c \cdot (\Gamma_s - cs) - k_{des} \cdot cs$		Surface reaction rate

*Variables 2*

- 1 On the **Home** toolbar, click **Variables** and choose **Local Variables**.
- 2 In the **Settings** window for Variables, locate the **Geometric Entity Selection** section.
- 3 From the **Geometric entity level** list, choose **Domain**.
- 4 Select Domain 1 only.

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

Name	Expression	Unit	Description
v_lam	$v_{\max} * (1 - ((x - 0.5 * \text{delta}) / (0.5 * \text{delta}))^2)$	m/s	Inlet velocity profile

## TRANSPORT OF DILUTED SPECIES (TDS)

### Transport Properties I

- 1 In the **Model Builder** window, under **Component 1 (comp1)>Transport of Diluted Species (tds)** click **Transport Properties I**.
- 2 In the **Settings** window for Transport Properties, locate the **Diffusion** section.
- 3 In the  $D_c$  text field, type D.
- 4 Locate the **Model Inputs** section. Specify the **u** vector as

0	x
v_lam	y

### Initial Values I

- 1 In the **Model Builder** window, under **Component 1 (comp1)>Transport of Diluted Species (tds)** click **Initial Values I**.
- 2 In the **Settings** window for Initial Values, locate the **Initial Values** section.
- 3 In the  $c$  text field, type  $c_0$ .

### Reactions I

- 1 On the **Physics** toolbar, click **Domains** and choose **Reactions**.
- 2 Select Domain 1 only.

### Concentration I

- 1 On the **Physics** toolbar, click **Boundaries** and choose **Concentration**.
- 2 Select Boundary 2 only.
- 3 In the **Settings** window for Concentration, locate the **Concentration** section.
- 4 Select the **Species c** check box.
- 5 In the  $c_{0,c}$  text field, type  $c_0$ .

### Flux I

- 1 On the **Physics** toolbar, click **Boundaries** and choose **Flux**.
- 2 Select Boundary 5 only.

- 3 In the **Settings** window for Flux, locate the **Inward Flux** section.
- 4 Select the **Species c** check box.
- 5 In the  $N_{0,c}$  text field, type -R.

#### *Outflow 1*

- 1 On the **Physics** toolbar, click **Boundaries** and choose **Outflow**.
- 2 Select Boundary 3 only.

#### *Symmetry 1*

- 1 On the **Physics** toolbar, click **Boundaries** and choose **Symmetry**.
- 2 Select Boundaries 1, 4, and 6 only.

Next, set up the equation and boundary conditions for the surface concentration, cs.

### **GENERAL FORM BOUNDARY PDE (GB)**

- 1 In the **Model Builder** window, under **Component 1 (comp1)** click **General Form Boundary PDE (gb)**.
- 2 In the **Settings** window for General Form Boundary PDE, locate the **Boundary Selection** section.
- 3 From the **Selection** list, choose **Manual**.
- 4 Click **Clear Selection**.
- 5 Select Boundary 5 only.
- 6 Locate the **Units** section. Find the **Dependent variable quantity** subsection. From the list, choose **None**.
- 7 In the **Unit** text field, type  $\text{mol}/\text{m}^2$ .
- 8 Find the **Source term quantity** subsection. In the **Unit** text field, type  $\text{mol}/(\text{m}^2 \cdot \text{s})$ .

#### *General Form PDE 1*

- 1 In the **Model Builder** window, under **Component 1 (comp1)**>**General Form Boundary PDE (gb)** click **General Form PDE 1**.
- 2 In the **Settings** window for General Form PDE, click to expand the **Equation** section. Comparing this equation with [Equation 1](#) in the [Model Definition](#) section leads to the following settings:

**3** Locate the **Conservative Flux** section. Specify the  $\Gamma$  vector as

-csTx*Ds	x
-csTy*Ds	y

Here, csTx and csTy refer to the components of the gradient  $\nabla c_s$  restricted to the plane tangential to the boundary where the interface is defined, that is, Boundary 5. Because this boundary is parallel to the y-axis, only csTy is nonzero in this case.

**4** Locate the **Source Term** section. In the  $f$  text field, type R.

#### *Initial Values*

The default initial value, 0, for the surface concentration applies for this model, so you do not need to set it explicitly.

## **MESH 1**

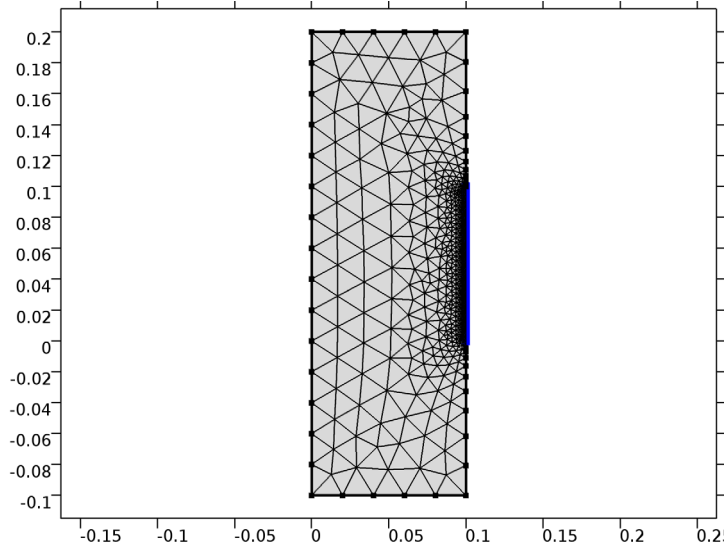
### *Free Triangular*

In the **Model Builder** window, under **Component 1 (comp1)** right-click **Mesh 1** and choose **Free Triangular**.

### *Size*

- 1** In the **Model Builder** window, under **Component 1 (comp1)>Mesh 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**.
- 4** Select Boundary 5 only.
- 5** Locate the **Element Size** section. Click the **Custom** button.
- 6** Locate the **Element Size Parameters** section. Select the **Maximum element size** check box.
- 7** In the associated text field, type 1.5[um].

8 Click the **Build All** button.



## STUDY I

### Step 1: Time Dependent

- 1 In the **Model Builder** window, expand the **Study I** node, then click **Step 1: Time Dependent**.
- 2 In the **Settings** window for Time Dependent, locate the **Study Settings** section.
- 3 In the **Times** text field, type range (0, 0.05, 2).
- 4 On the **Home** toolbar, click **Compute**.

## RESULTS

### Concentration (tds)

- 1 Click the **Zoom Extents** button on the **Graphics** toolbar.

The first default plot shows the concentration of the reacting species at the end of the simulation interval,  $t = 2$  s.

### 1D Plot Group 3

Create a plot of the final concentration at the reacting surface.

- 1 On the **Home** toolbar, click **Add Plot Group** and choose **1D Plot Group**.
- 2 In the **Settings** window for 1D Plot Group, locate the **Data** section.

- 3 From the **Time selection** list, choose **From list**.
- 4 In the **Times (s)** list, select **2**.
- 5 On the **ID Plot Group 3** toolbar, click **Line Graph**.
- 6 Select Boundary 5 only.
- 7 In the **Settings** window for Line Graph, click **Replace Expression** in the upper-right corner of the **x-axis data** section. From the menu, choose **Geometry>Coordinate>y - y-coordinate**.
- 8 On the **ID Plot Group 3** toolbar, click **Plot**.

The plot should look like that in [Figure 3](#)

Proceed to reproduce the plot in [Figure 4](#) showing the concentration of adsorbed species at selected times. You can use the plot group you just created as the starting point.

#### *ID Plot Group 4*

- 1 In the **Model Builder** window, right-click **ID Plot Group 3** and choose **Duplicate**.
- 2 In the **Settings** window for ID Plot Group, locate the **Data** section.
- 3 In the **Times (s)** list, choose **0.05, 0.5, 1, 1.5, and 2**.
- 4 In the **Model Builder** window, expand the **ID Plot Group 4** node, then click **Line Graph 1**.
- 5 In the **Settings** window for Line Graph, click **Replace Expression** in the upper-right corner of the **y-axis data** section. From the menu, choose **Component 1>General Form Boundary PDE>cs - Dependent variable cs**.
- 6 On the **ID Plot Group 4** toolbar, click **Plot**.

Finally, reproduce the plot in [Figure 5](#) of the surface reaction rate at the same times. Again, use the previous plot group as the starting point.

#### *ID Plot Group 5*

- 1 In the **Model Builder** window, right-click **ID Plot Group 4** and choose **Duplicate**.
- 2 In the **Model Builder** window, expand the **ID Plot Group 5** node, then click **Line Graph 1**.
- 3 In the **Settings** window for Line Graph, click **Replace Expression** in the upper-right corner of the **y-axis data** section. From the menu, choose **Component 1>Definitions>Variables>R - Surface reaction rate**.
- 4 On the **ID Plot Group 5** toolbar, click **Plot**.

