

# Hydrogen Diffusion in Metals

Hydrogen embrittlement refers to the degradation of metal ductility due to the absorption of hydrogen. The metal becomes more brittle and thus cracks might initiate at lower stress levels. It is important to estimate hydrogen concentration and the speed at which it diffuses into the metal in order to predict and avoid crack formation and propagation.

This model shows how to simulate the uptake and diffusion of hydrogen in a notched metal sample from an aqueous electrolyte. It uses the Transport in Solids interface to model both the concentration-driven and stress-driven diffusion in a solid.

## Model Definition

The model geometry consists of a metal part with an initial defect as depicted in Figure 1.

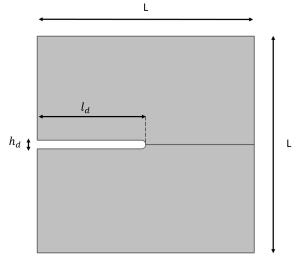


Figure 1: Model geometry.

The part size is L = 20 mm, and the defect is  $h_d = 0.4$  mm wide and extends for  $l_{\rm d}$  = 10 mm into the specimen.

The electrolyte is located on the left side of the metal part and a hydrogen influx is assigned on the boundary where the solid is in contact with it. The initial defect is also filled with electrolyte.

The solid is constrained on the bottom and right edges with a roller boundary condition. A prescribed displacement of 0.05 mm is applied on the top boundary to produce a state of stress and study its effect on hydrogen diffusion. Although not considered in this example, the symmetry about the *xz*-plane through the defect could be exploited to reduce the computational size.

The hydrogen diffusion is studied using the mass balance equation

$$\frac{\partial c}{\partial t} = -\nabla \cdot \Gamma + G$$

where c is the concentration (SI unit: mol/m<sup>3</sup>),  $\Gamma$  is the molar flux, and G is a source term. Following Ref. 1, hydrogen can be present both in the interstitial metal lattice and in traps,

$$c = c_1 + \sum_{i} c_{t, i}$$

To study the diffusion of the hydrogen in the interstitial lattice, the mass balance equation is rewritten as follows,

$$\frac{\partial c_{\mathbf{l}}}{\partial t} = -\nabla \cdot \Gamma + G - \left(\frac{\partial c_{\mathbf{t},\mathbf{l}}}{\partial t} + \frac{\partial c_{\mathbf{t},2}}{\partial t}\right)$$

where only two trap types are considered. A relation between the trap and lattice concentration can be found assuming a low lattice occupancy, see Ref. 1 for details.

Both the concentration gradient (Fick's law) and the stress gradient drive the diffusion of hydrogen in the metal,

$$\Gamma = -D\nabla c_{l} + \frac{Dc_{l}\Omega_{H}}{RT}\nabla\sigma_{h}$$

where D is the lattice diffusion coefficient,  $\Omega_{\rm H}$  is the partial molar volume of hydrogen, and  $\sigma_{\rm h} = \frac{1}{3} {\rm tr}(\sigma)$  is the hydrostatic stress. The electrolyte and the chemical reactions therein are not modeled explicitly; instead an approximation for the flux as a function of the pH and the electrolyte potential,  $V_{\rm e}$ , is used (Ref. 1),

$$\begin{split} j &= -\Gamma \cdot \mathbf{N} = & (1-\theta)(k_{\mathrm{va}}c_{\mathrm{H}} \mathrm{exp}(-\alpha_{\mathrm{va}}\eta) + k_{\mathrm{vb}} \mathrm{exp}(-\alpha_{\mathrm{vb}}\eta)) \\ & -\theta(k_{\mathrm{ha}}c_{\mathrm{H}} \mathrm{exp}(-\alpha_{\mathrm{ha}}\eta) + k_{\mathrm{hb}} \mathrm{exp}(-\alpha_{\mathrm{hb}}\eta) + 2k_{\mathrm{T}}\theta) \end{split}$$

where

$$\eta = \frac{(V_{\rm m} - V_{\rm eq} - V_{\rm e})F}{RT},$$

$$\theta = \frac{c_1}{\frac{k_a}{k_{ar}}(N - c_1) + c_1},$$

and

$$c_{\rm H} = 10^{-\,{\rm pH} + 3}$$

The electrolyte parameters used in the influx expression are inspired from Ref. 1 and reported in Table 1.

TABLE I: MODEL PARAMETERS.

Parameter	Value
Diffusion coefficient (D)	2E-9 m <sup>2</sup> /s
Metal potential (V <sub>m</sub> )	-0.5 V
Equilibrium potential (V <sub>eq</sub> )	0 V
Electrolyte potential (V <sub>e</sub> )	-0.025 V
Hydrogen partial molar volume ( $\Omega_{ m H}$ )	2E-6 m <sup>3</sup> /mol
Temperature (T)	293.15 K
Volmer forward reaction coefficient, acid $(\alpha_{\text{va}})$	0.48
Volmer forward reaction coefficient, basic ( $\alpha_{\rm vb}$ )	0.48
Heyrovsky forward reaction coefficient, acid ( $\alpha_{\rm ha}$ )	0.33
Heyrovsky forward reaction coefficient, basic $(\alpha_{\mbox{\scriptsize hb}})$	0.33
Volmer forward reaction rate, acid (k <sub>va</sub> )	IE-4 m/s
Volmer forward reaction rate, basic $(k_{vb})$	IE-8 mol/m <sup>2</sup> s
Heyrovsky forward reaction rate, acid (k <sub>ha</sub> )	IE-10 m/s
Heyrovsky forward reaction rate, basic (k <sub>hb</sub> )	9E-10 mol/m <sup>2</sup> s
Tafel forward reaction rate $(k_T)$	IE-6 mol/m <sup>2</sup> s
Absorption forward reaction rate (k <sub>a</sub> )	IE5 m/s
Absorption backward reaction rate (k <sub>ar</sub> )	9E9 m/s
Lattice sites concentration (N)	le6 mol/m <sup>3</sup>
Trap I concentration (ntl)	2 mol/m <sup>3</sup>
Trap 2 concentration (n <sub>t2</sub> )	I mol/m <sup>3</sup>
pH	13

Figure 2 shows the concentration and the flux direction of the hydrogen after 2 hours. The concentration is higher at the sharp corner of the crack because of the greater area exposed to the electrolyte.

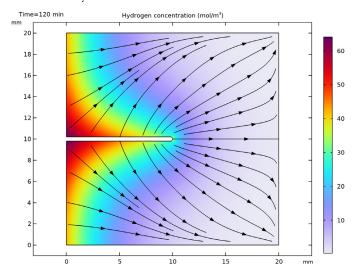
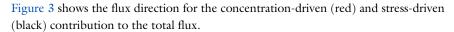


Figure 2: Hydrogen concentration and hydrogen flux after 2 hours.



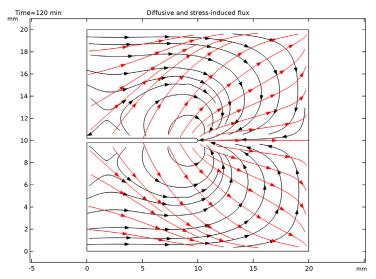


Figure 3: Streamline plot of the concentration-driven (red) and stress-driven (black) hydrogen flux.

The effect of the stress on hydrogen absorption can be seen in Figure 4. The figure compares the time evolution of the hydrogen concentration at the tip of the defect with and without the stress contribution to the flux. The stress-induced flux increases the absorption of hydrogen.

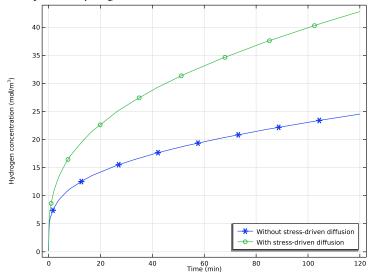


Figure 4: Hydrogen concentration with and without stress contribution to the diffusion flux at the tip of the defect.

The hydrogen concentration in the metal part along the centerline is shown in Figure 5 for both cases.

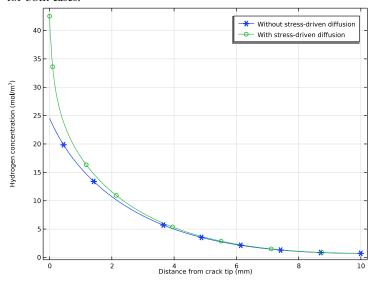


Figure 5: Hydrogen diffusion depth along the centerline of the specimen.

Figure 6 below shows the hydrostatic stress and the deformed geometry. There is a stress concentration at the crack tip, which enhances the hydrogen adsorption

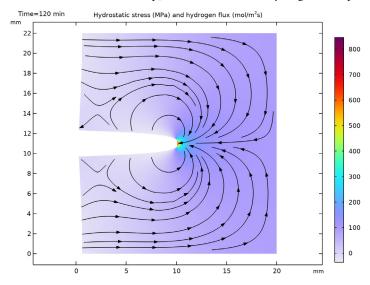


Figure 6: Hydrostatic stress and hydrogen flux in the deformed configuration (100 times amplified).

# Notes About the COMSOL Implementation

The stress-driven diffusion can be included through the External Flux subfeature. A parametric study is used to evaluate the solution with and without the additional flux due to the hydrostatic stress gradient.

# Reference

1. T. Hageman and E. Martinez-Paneda, An electro-chemo-mechanical framework for predicting hydrogen uptake in metals due to aqueous electrolytes, Corrosion Science, vol. 208, 110681, 2022

Application Library path: Structural\_Mechanics\_Module/Diffusion\_in\_Solids/ hydrogen diffusion

From the File menu, choose New.

#### NEW

In the New window, click Model Wizard.

#### MODEL WIZARD

- I In the Model Wizard window, click **2** 2D.
- 2 In the Select Physics tree, select Structural Mechanics>Solid Mechanics (solid).
- 3 Click Add.
- 4 In the Select Physics tree, select Chemical Species Transport>Transport in Solids (ts).
- 5 Click Add.
- 6 Click Study.
- 7 In the Select Study tree, select General Studies>Time Dependent.
- 8 Click **Done**.

#### **GLOBAL DEFINITIONS**

#### Geometric Parameters

- I In the Model Builder window, under Global Definitions click Parameters I.
- 2 In the Settings window for Parameters, locate the Parameters section.
- **3** In the table, enter the following settings:

Name	Expression	Value	Description
L	20[mm]	0.02 m	Domain size
Ld	10[mm]	0.01 m	Defect length
Hd	0.4[mm]	4E-4 m	Defect height

4 In the Label text field, type Geometric Parameters.

#### Model Parameters

- I In the Home toolbar, click Pi Parameters and choose Add>Parameters.
- 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 hydrogen\_diffusion\_parameters.txt.

5 In the Label text field, type Model Parameters.

#### **GEOMETRY I**

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

#### Metal Domain

- I In the Geometry toolbar, click Square.
- 2 In the Settings window for Square, locate the Size section.
- 3 In the Side length text field, type L.
- 4 Click to expand the Layers section. In the table, enter the following settings:

Layer name	Thickness (mm)	
Layer 1	L/2	

5 In the Label text field, type Metal Domain.

## Fracture

- I 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 Ld.
- **4** In the **Height** text field, type Hd.
- 5 Locate the **Position** section. In the y text field, type (L-Hd)/2.
- 6 In the Label text field, type Fracture.

## Fracture Fillet

- I In the Geometry toolbar, click **Fillet**.
- 2 On the object r1, select Points 2 and 3 only.
- 3 In the Settings window for Fillet, locate the Radius section.
- 4 In the Radius text field, type Hd/2.
- 5 In the Label text field, type Fracture Fillet.

#### Remove Fracture

- I In the Geometry toolbar, click Booleans and Partitions and choose Difference.
- 2 Select the object sql 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 object **fill** only.
- 6 In the Label text field, type Remove Fracture.
- 7 Click Build All Objects.

#### ADD MATERIAL

- I In the Home toolbar, click Radd Material to open the Add Material window.
- 2 Go to the Add Material window.
- 3 In the tree, select Built-in>Iron.
- 4 Click Add to Component in the window toolbar.
- 5 In the Home toolbar, click 4 Add Material to close the Add Material window.

## SOLID MECHANICS (SOLID)

Prescribed Displacement: Top

- I In the Model Builder window, under Component I (compl) right-click Solid Mechanics (solid) and choose Prescribed Displacement.
- 2 Click the **Zoom Extents** button in the **Graphics** toolbar.
- **3** Select Boundary 6 only.
- 4 In the Settings window for Prescribed Displacement, locate the Prescribed Displacement section.
- 5 From the Displacement in y direction list, choose Prescribed.
- **6** In the  $u_{0y}$  text field, type U0.
- 7 In the Label text field, type Prescribed Displacement: Top.

## Roller I

- I In the Physics toolbar, click Boundaries and choose Roller.
- 2 Select Boundaries 2, 8, and 9 only.

#### DEFINITIONS

Define an **Analytic** function for the trap contribution, see Ref. 1 for details.

## Trap Contribution

- I In the Home toolbar, click f(x) Functions and choose Local>Analytic.
- 2 In the Settings window for Analytic, locate the Definition section.

- 3 In the Expression text field, type (NT/N)\*exp(Eb/(R\_const\*T0))/((1+(max(cl,0)/N)\*exp(Eb/(R const\*T0)))^2).
- 4 In the Arguments text field, type cl, NT, Eb.
- **5** Locate the **Units** section. In the **Function** text field, type 1.
- **6** In the table, enter the following settings:

Argument	Unit	
cl	mo1/m^3	
NT	mo1/m^3	
Eb	kJ/mol	

- 7 In the Function name text field, type trapFun.
- 8 In the Label text field, type Trap Contribution.

#### Variables 1

- I In the Model Builder window, right-click Definitions and choose Variables.
- 2 In the Settings window for Variables, locate the Variables section.
- 3 Click Load from File.
- **4** Browse to the model's Application Libraries folder and double-click the file hydrogen\_diffusion\_variables.txt.

#### Influx Boundary Selection

- I In the **Definitions** toolbar, click **\( \bigcap\_{\bigcap} \) Explicit**.
- 2 In the Settings window for Explicit, locate the Input Entities section.
- 3 From the Geometric entity level list, choose Boundary.
- 4 Select Boundaries 1, 3–5, 10, and 11 only.
- 5 In the Label text field, type Influx Boundary Selection.

#### TRANSPORT IN SOLIDS (TS)

Add the stress gradient contribution as an external flux in the material frame. Multiply the flux definition with the parameter para to be able to activate and deactivate the stress-driven flux in a parametric study.

## Solid 1

- I In the Model Builder window, under Component I (compl)>Transport in Solids (ts) click Solid I.
- 2 In the Settings window for Solid, locate the Diffusion section.

**3** In the  $D_{\rm c}$  text field, type D.

## External Flux I

- I In the Physics toolbar, click Attributes and choose External Flux.
- 2 In the Settings window for External Flux, locate the External Flux section.
- **3** Select the **Species c** check box.
- 4 Click to expand the Advanced section. From the Frame list, choose Reference configuration.
- **5** Locate the **External Flux** section. In the  $\Gamma_{\text{ext.c}}$  table, enter the following settings:

```
D_sigma*d(-solid.pm,X)*para
D_sigma*d(-solid.pm,Y)*para
```

## Source: Hydrogen Traps

- I In the Physics toolbar, click **Domains** and choose **Source**.
- 2 Click in the **Graphics** window and then press Ctrl+A to select both domains.
- 3 In the Settings window for Source, locate the Sources section.
- **4** In the  $S_{\rm c}$  text field, type -srcCoeff\*cTIME.
- 5 In the Label text field, type Source: Hydrogen Traps.

#### Flux I

- I In the Physics toolbar, click Boundaries and choose Flux.
- 2 In the Settings window for Flux, locate the Boundary Selection section.
- 3 From the Selection list, choose Influx Boundary Selection.
- **4** Locate the **Inward Flux** section. In the  $\gamma_{0,c}$  text field, type J\_influx.

#### MESH I

Due to symmetry, you can mesh half the geometry and use the **Copy Domain** node to copy the mesh to the other half.

## Free Quad I

- I In the Mesh toolbar, click Free Quad.
- 2 In the Settings window for Free Quad, locate the Domain Selection section.
- 3 From the Geometric entity level list, choose Domain.
- 4 Select Domain 2 only.

#### Distribution I

I Right-click Free Quad I and choose Distribution.

- **2** Select Boundary 5 only.
- 3 In the Settings window for Distribution, locate the Distribution section.
- 4 From the Distribution type list, choose Predefined.
- 5 In the Number of elements text field, type 40.
- 6 In the Element ratio text field, type 2.

#### Distribution 2

- I In the Model Builder window, right-click Free Quad I and choose Distribution.
- **2** Select Boundary 7 only.
- 3 In the Settings window for Distribution, locate the Distribution section.
- 4 From the Distribution type list, choose Predefined.
- **5** In the **Number of elements** text field, type 60.
- 6 In the Element ratio text field, type 10.
- 7 From the Growth rate list, choose Exponential.

#### Size

- I In the Model Builder window, under Component I (compl)>Mesh I click Size.
- 2 In the Settings window for Size, locate the Element Size section.
- 3 From the Predefined list, choose Extra fine.

#### Copy Domain I

- I In the Model Builder window, right-click Mesh I and choose Copying Operations> Copy Domain.
- 2 Select Domain 2 only.
- 3 In the Settings window for Copy Domain, locate the Destination Domains section.
- **4** Click to select the **Activate Selection** toggle button.
- **5** Select Domain 1 only.
- 6 Click III Build All.

#### STUDY I

#### Step 1: Time Dependent

- I In the Model Builder window, under Study I click Step I: Time Dependent.
- 2 In the Settings window for Time Dependent, locate the Study Settings section.
- **3** From the **Time unit** list, choose **min**.

4 In the Output times text field, type 0 10^{range(log10(1/60),1/10,log10(120))} 120.

#### Parametric Sweep

Add a **Parametric Sweep** to activate and deactivate the stress-driven flux contribution.

- I In the Study toolbar, click Parametric Sweep.
- 2 In the Settings window for Parametric Sweep, locate the Study Settings section.
- 3 Click + Add.
- **4** In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
para (Activation parameter)	0 1	

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

#### RESULTS

#### Hydrostatic Stress

- I In the Settings window for 2D Plot Group, type Hydrostatic Stress in the Label text field.
- 2 Click to expand the Title section. From the Title type list, choose Manual.
- 3 In the Title text area, type Hydrostatic stress (MPa) and hydrogen flux (mol/ m < sup > 2 < / sup > s).
- 4 In the Parameter indicator text field, type Time=eval(t,min) min.
- 5 Locate the Plot Settings section. Clear the Plot dataset edges check box.

#### Surface I

- I In the Model Builder window, expand the Hydrostatic Stress node, then click Surface I.
- 2 In the Settings window for Surface, locate the Expression section.
- **3** In the **Expression** text field, type -solid.pm.
- 4 From the Unit list, choose MPa.

## Deformation

- I In the Model Builder window, expand the Surface I node, then click Deformation.
- 2 In the Settings window for Deformation, locate the Scale section.
- **3** Select the **Scale factor** check box. In the associated text field, type 100.

#### Streamline 1

- I In the Model Builder window, right-click Hydrostatic Stress and choose Streamline.
- 2 In the Settings window for Streamline, locate the Expression section.
- 3 In the X-component text field, type ts.extflux\_cx.
- 4 In the **Y-component** text field, type ts.extflux\_cy.
- 5 In the Hydrostatic Stress toolbar, click Plot.
- 6 Locate the Streamline Positioning section. From the Positioning list, choose Uniform density.
- 7 Locate the Coloring and Style section. Find the Point style subsection. From the Type list, choose Arrow.
- 8 Click to expand the Inherit Style section. From the Plot list, choose Surface 1.

## Deformation I

- I Right-click Streamline I and choose Deformation.
- 2 In the Hydrostatic Stress toolbar, click Plot.

#### Concentration

- I In the Model Builder window, under Results click Transported Quantity (ts).
- 2 In the Settings window for 2D Plot Group, locate the Title section.
- 3 From the Title type list, choose Manual.
- 4 In the Title text area, type Hydrogen concentration (mol/m<sup>3</sup>).
- 5 In the Parameter indicator text field, type Time=eval(t,min) min.
- **6** In the **Label** text field, type Concentration.

#### Surface I

- I In the Model Builder window, expand the Concentration node, then click Surface I.
- 2 In the Settings window for Surface, locate the Coloring and Style section.
- 3 Click Change Color Table.
- 4 In the Color Table dialog box, select Rainbow>Prism in the tree.
- 5 Click OK.

#### Streamline 1

- I In the Model Builder window, click Streamline I.
- 2 In the Settings window for Streamline, locate the Coloring and Style section.
- 3 Find the Point style subsection. From the Color list, choose Black.
- 4 From the Arrow length list, choose Normalized.

- **5** Locate the **Inherit Style** section. From the **Plot** list, choose **Surface 1**.
- 6 In the Concentration toolbar, click Plot.

#### Diffusive and Stress-Induced Flux

Add a plot to visualize the concentration-driven and stress-driven hydrogen flux.

- I In the Home toolbar, click Add Plot Group and choose 2D Plot Group.
- 2 In the Settings window for 2D Plot Group, locate the Data section.
- 3 From the Dataset list, choose Study I/Parametric Solutions I (sol2).
- 4 Locate the Title section. From the Title type list, choose Manual.
- 5 In the Title text area, type Diffusive and stress-induced flux.
- 6 In the Parameter indicator text field, type Time=eval(t,min) min.
- 7 In the Label text field, type Diffusive and Stress-Induced Flux.

#### Streamline 1

- I Right-click Diffusive and Stress-Induced Flux and choose Streamline.
- 2 In the Settings window for Streamline, locate the Expression section.
- 3 In the X-component text field, type ts.extflux cx.
- 4 In the **Y-component** text field, type ts.extflux cy.
- 5 Locate the Streamline Positioning section. From the Positioning list, choose Uniform density.
- 6 Locate the Coloring and Style section. Find the Point style subsection. From the Type list, choose Arrow.
- 7 Right-click Streamline I and choose Duplicate.

### Streamline 2

- I In the Model Builder window, click Streamline 2.
- 2 In the Settings window for Streamline, locate the Expression section.
- 3 In the X-component text field, type ts.dflux cx.
- 4 In the **Y-component** text field, type ts.dflux\_cy.
- 5 Locate the Coloring and Style section. Find the Point style subsection. From the Color list, choose Red.
- 6 In the Diffusive and Stress-Induced Flux toolbar, click Plot.
- 7 Click the **Zoom Extents** button in the **Graphics** toolbar.

Hydrogen Concentration in Metal

Add a plot to visualize the hydrogen concentration along the centerline of the solid with and without considering stress-driven diffusion.

- I In the Home toolbar, click Add Plot Group and choose ID Plot Group.
- 2 In the Settings window for ID Plot Group, locate the Data section.
- 3 From the Dataset list, choose Study I/Parametric Solutions I (sol2).
- **4** From the **Time selection** list, choose **Last**.
- **5** Click to expand the **Title** section. From the **Title type** list, choose **None**.
- 6 Locate the Plot Settings section.
- 7 Select the x-axis label check box. In the associated text field, type Distance from crack tip (mm).
- 8 Select the y-axis label check box. In the associated text field, type Hydrogen concentration (mol/m<sup>3</sup>).
- 9 In the Label text field, type Hydrogen Concentration in Metal.

## Line Graph 1

- I Right-click Hydrogen Concentration in Metal and choose Line Graph.
- **2** Select Boundary 7 only.
- 3 In the Settings window for Line Graph, locate the y-Axis Data section.
- 4 In the **Expression** text field, type c.
- **5** Click to expand the **Legends** section. Select the **Show legends** check box.
- 6 From the Legends list, choose Manual.
- 7 In the table, enter the following settings:

# Legends Without stress-driven diffusion With stress-driven diffusion

- 8 Click to expand the Coloring and Style section. Find the Line markers subsection. From the Marker list, choose Cycle.
- **9** From the **Positioning** list, choose **Interpolated**.

Hydrogen Concentration at Crack Tip

Add a plot to visualize the hydrogen concentration at the crack tip as a function of time.

- I In the Home toolbar, click Add Plot Group and choose ID Plot Group.
- 2 In the Settings window for ID Plot Group, locate the Data section.
- 3 From the Dataset list, choose Study I/Parametric Solutions I (sol2).
- 4 Locate the Title section. From the Title type list, choose None.
- 5 Locate the Plot Settings section.
- 6 Select the y-axis label check box. In the associated text field, type Hydrogen concentration (mol/m<sup>3</sup>).
- 7 In the Label text field, type Hydrogen Concentration at Crack Tip.
- 8 Locate the Legend section. From the Position list, choose Lower right.

## Point Graph 1

- I Right-click Hydrogen Concentration at Crack Tip and choose Point Graph.
- **2** Select Point 7 only.
- 3 In the Settings window for Point Graph, locate the y-Axis Data section.
- 4 In the Expression text field, type c.
- 5 Locate the x-Axis Data section. From the Unit list, choose min.
- 6 Click to expand the Coloring and Style section. Find the Line markers subsection. From the Marker list, choose Cycle.
- 7 From the Positioning list, choose Interpolated.
- 8 Click to expand the **Legends** section. Select the **Show legends** check box.
- 9 From the Legends list, choose Manual.
- **10** In the table, enter the following settings:

Legends
Without stress-driven diffusion
With stress-driven diffusion

II In the Hydrogen Concentration at Crack Tip toolbar, click **Tip** Plot.