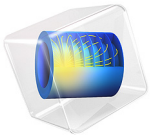

Neutralization of Chlorine in a Scrubber

Introduction

This application studies the kinetics of the neutralization of chlorine gas in water solution. It assumes that the fluid volume is perfectly mixed and constant. This means that the chlorine has dissolved to an almost saturated state (1×10^{-2} mol/m^3) and that the hydroxide has also mixed well throughout, as would be the case for a very small amount of fluid in a scrubber. The study allows investigation of the time-scale of the reactions and the concentrations of the resulting products. A study of this type can be useful to determine the amount of hydroxide required to neutralize the chlorine and for sizing of a chlorine scrubber.

The example illustrates the functionality of the Reaction Engineering interface available in the Chemical Reaction Engineering Module to study chemical processes involving several equilibrium reactions.

Model Definition

The model includes four reactions that take place in a constant volume batch reactor. The reaction rates are very fast for these reactions, and they can be seen as equilibrium reactions.

Chlorine neutralization by hydroxide ions:

$$Cl_2 + OH^- \underset{k^r}{\overset{k^f}{\rightleftharpoons}} HClO + Cl^- \tag{1}$$

Autoionization of water:

$$H_2O \overset{K^{eq}}{\rightleftharpoons} H^+ + OH^- \tag{2}$$

Formed hypochlorous acid reacting with hydroxide ions:

$$HClO + OH^- \overset{K^{eq}}{\rightleftharpoons} ClO^- + H_2O \tag{3}$$

Chlorine reaction with water:

$$Cl_2 + H_2O \underset{k^r}{\overset{k^f}{\rightleftharpoons}} ClO^- + Cl^- + 2H^+ \tag{4}$$

Traditionally, when setting up the reaction terms and mass balances of a reaction scheme, a full description of the mass action law is required. This includes reaction rate constants for both the forward and reverse reactions in the reaction term and subsequent mass balances. In the present example, you can assume that the forward and reverse reaction rate constants for Equation 2 and Equation 3 are not available, and that you have to use equilibrium constants instead. This is easily achieved using the Reaction Engineering interface.

The thermodynamic and kinetic data for the system are found in Ref. 1 and Ref. 2. These are listed in Table 1 below.

TABLE 1: KINETIC PARAMETERS FOR THE NEUTRALIZATION REACTIONS.

REACTION	k^f	k^r	K^{eq}
Equation 1	$1.565 \cdot 10^{6}$	$3.485 \cdot 10^{-5}$	
Equation 2			$1 \cdot 10^{8}$
Equation 3			$2.79 \cdot 10^{3}$
Equation 4	16.48	$3.7 \cdot 10^{-10}$	

There are eight species participating in the reactions, of which one — H_2O is the solvent. The parameters in Table 1 are valid for a solvent concentration set to unity. The only other non-vanishing initial concentration is that for chlorine in water, which is set to the value of $1 \cdot 10^{-2}$ mol/m^3. Yet, it is always useful to avoid zero concentrations throughout a specified reaction model, because they often show up in the participating equations, such as in those describing equilibrium. Therefore, some arbitrary trace concentrations are entered for the other species.

Results

Figure 1 shows the concentration profile during the first second of reaction.

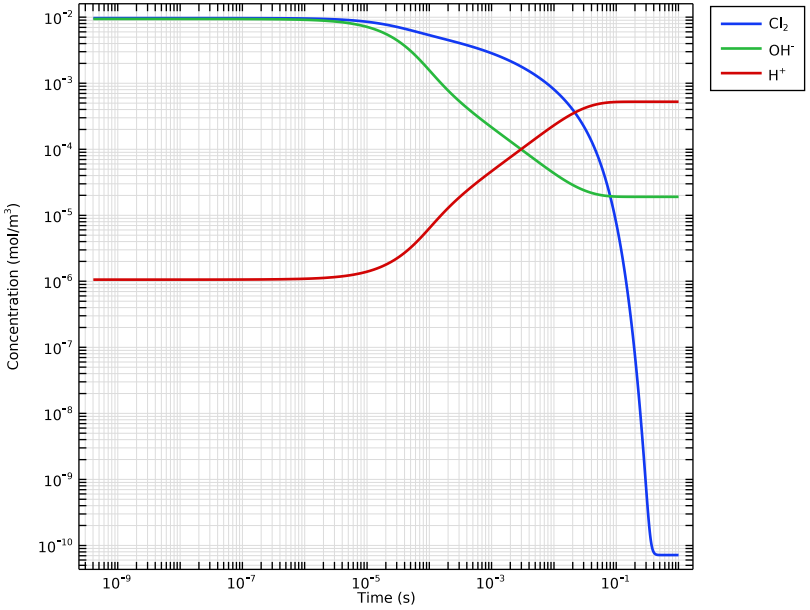

Figure 1: Dissolved chlorine (aq), hydrogen ion, and hydroxide ion concentration in a log scale versus logarithmic time graph.

Initially, the chlorine quickly decays through the ready abundance of hydroxide ions. It continues to be reduced at a slower pace through the reaction with hydroxide ions that are, in turn, being produced through the water dissociation reaction. The initial concentration of the hydroxide ions is sufficiently large to guarantee an alkaline final solution.

A basic conclusion that can be drawn from this figure, is that a contact time of at least 150 ms is required to reduce the chlorine concentration to levels below 10^{-6} mol/m^3. This is quite a short time in comparison with, for example, the time scale associated with the transport of chlorine into water.

References

1. C.W. Spalding, "Reaction Kinetics in the Absorption of Chlorine into Aqueous Media, " *AIChE J.*, vol. 8, no. 5, pp. 685–689, 1962.

2. S.S. Ashour, E.B. Rinker, and O.C. Sandall, *Absorption of Chlorine into Aqueous Bicarbonate Solutions and Aqueous Hydroxide Solutions*, AIChE J., 42, 671, 1996.

Application Library path: `Chemical_Reaction_Engineering_Module/Ideal_Tank_Reactors/chlorine_scrubber`

Modeling Instructions

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

NEW

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

MODEL WIZARD

1. In the **Model Wizard** window, The model utilizes the **Reaction Engineering** interface with a time-dependent study.
2. click **0D**.
3. In the **Select Physics** tree, select **Chemical Species Transport>Reaction Engineering (re)**.
4. Click **Add**.
5. Click **Study**.
6. In the **Select Study** tree, select **General Studies>Time Dependent**.
7. Click **Done**.

GLOBAL DEFINITIONS

Start by reading in a set of global parameters.

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 `chlorine_scrubber_parameters.txt`.

The default reactor type, Batch, constant volume, is used in this study. The reactions are studied for isothermal condition.

REACTION ENGINEERING (RE)

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Reaction Engineering (re)**.

2 In the **Settings** window for **Reaction Engineering**, locate the **Energy Balance** section.

3 In the T text field, type `Temp`.

4 Click to expand the **Mixture Properties** section. From the **Phase** list, choose **Liquid**.

Set up each of the reactions and enter the reaction parameters. Use the default reaction rate expressions.

Reaction 1

1 In the **Reaction Engineering** toolbar, click **Reaction**.

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

3 In the **Formula** text field, type `Cl2+OH-<=>HClO+Cl-`.

4 Click **Apply**.

5 Click **Balance** in the upper-right corner of the **Reaction Formula** section.

6 Locate the **Rate Constants** section. In the k^{f} text field, type `kfreac_1`.

7 In the k^{r} text field, type `krreac_1`.

Reaction 2

1 In the **Reaction Engineering** toolbar, click **Reaction**.

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

3 In the **Formula** text field, type `OH-+H+=H2O`.

4 Click **Apply**.

5 Click **Balance** in the upper-right corner of the **Reaction Formula** section.

6 Locate the **Equilibrium Settings** section. In the K_{eq0} text field, type `Kequi_2`.

Species: H2O

H2O is in great excess and acts as solvent.

1 In the **Model Builder** window, click **Species: H2O**.

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

3 From the list, choose **Solvent**.

Reaction 3

1 In the **Reaction Engineering** toolbar, click **Reaction**.

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

3 In the **Formula** text field, type `HClO+OH-=ClO-+H2O`.

4 Click **Apply**.

5 Click **Balance** in the upper-right corner of the **Reaction Formula** section.

6 Locate the **Equilibrium Settings** section. In the K_{eq0} text field, type `Kequi_3`.

Reaction 4

1 In the **Reaction Engineering** toolbar, click **Reaction**.

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

3 In the **Formula** text field, type `Cl2+H2O<=>ClO-+Cl-+H+`.

4 Click **Apply**.

5 Click **Balance** in the upper-right corner of the **Reaction Formula** section.

6 Locate the **Rate Constants** section. In the k^{f} text field, type `kfreac_4`.

7 In the k^{r} text field, type `krreac_4`.

Initial Values 1

Set the initial conditions. For stability reasons, set a very low concentration instead of zero concentration for species that should not be present in the system initially.

1 In the **Model Builder** window, click **Initial Values 1**.

2 In the **Settings** window for **Initial Values**, locate the **Volumetric Species Initial Values** section.

3 In the table, enter the following settings:

Species	Concentration (mol/m^3)
Cl-	`cCl_0`
Cl2	`cCl2_0`
ClO-	`cClO_0`
H+	`cH_0`
H2O	`cH2O_0`
HClO	`cHClO_0`
OH-	`cOH_0`

STUDY 1

In the **Home** toolbar, click **Compute**.

RESULTS

Concentration (re)

Follow these steps to generate Figure 1.

1. In the **Settings** window for **1D Plot Group**, locate the **Axis** section.
2. Select the **x-axis log scale** check box.
3. Select the **y-axis log scale** check box.
4. Locate the **Legend** section. From the **Layout** list, choose **Outside graph axis area**.

Global 1

1. In the **Model Builder** window, expand the **Concentration (re)** node, then click **Global 1**.
2. In the **Settings** window for **Global**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)> Reaction Engineering>re.c_Cl2 - Concentration - mol/m³**.
3. Click **Add Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)>Reaction Engineering>re.c_OH_1m - Concentration - mol/m³**.
4. Click **Add Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)>Reaction Engineering>re.c_H_1p - Concentration - mol/m³**.
5. Click to expand the **Coloring and Style** section. From the **Width** list, choose **2**.
6. Click to expand the **Legends** section. From the **Legends** list, choose **Manual**.
7. In the table, enter the following settings:

Legends
Cl₂
OH⁻
H⁺

Concentration (re)

1. In the **Model Builder** window, click **Concentration (re)**.
2. In the **Concentration (re)** toolbar, click **Plot**.
3. Click the **Zoom Extents** button in the **Graphics** toolbar.