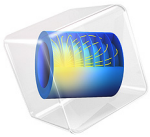


Finding Kinetic Arrhenius Parameters Using Parameter Estimation

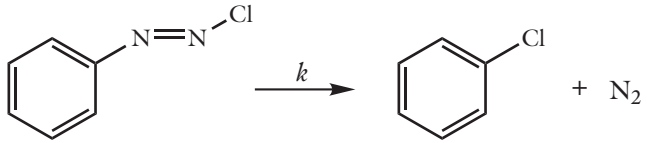
Introduction

This example shows how to use the Parameter Estimation feature in the Reaction Engineering interface to find the Arrhenius parameters of a first order reaction. Inspiration for this example is taken from Ref. 1.

Note: This example requires the Optimization Module.

Model Definition

Benzene diazonium chloride in the gas phase decomposes to benzene chloride and nitrogen according to



The reaction is first order with the rate:

$$r = kc_{\mathrm{PhN2Cl}}$$

where the temperature dependent rate constant given by

$$k = A\exp\left(-\frac{E}{R_g T}\right)$$

Above, A is the frequency factor (SI unit: 1/s) and E is the activation energy (SI unit: J/mol).

In order to evaluate the Arrhenius parameters, A and E, a set of experiments was conducted using a perfectly mixed isothermal batch system with constant volume. The concentration of benzene diazonium chloride was monitored as function of time for the temperatures; T = 313 K, 319 K, 323 K, 328 K, and 333 K.

The model optimizes A and E at these temperatures with the Parameter Estimation feature for simulations utilizing the isothermal constant volume Batch reactor type. Five experimental datasets are available in the model file as *comma-separated value* files (*csv*-files).

Parameter estimation calculations give the values $A = 1.27 \cdot 10^{16}$ (SI unit: 1/s) and $E = 116$ (SI unit: kJ/mol) for the frequency factor and activation energy, respectively. Figure 1 plots the model results and the associated experimental data points.

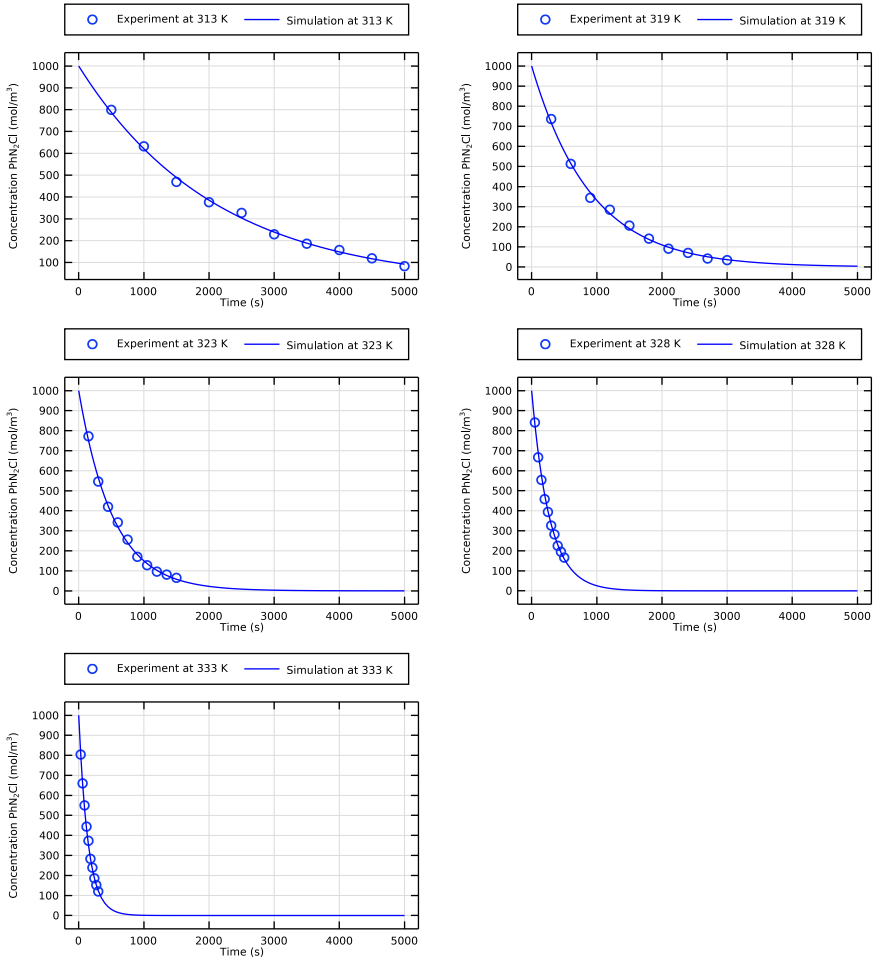


Figure 1: Model results and experimental data for PhN_2Cl concentration as a function of time.

Notes About the COMSOL Implementation

The parameter estimation solver is more efficient in finding an optimal parameter set if the model experiences similar sensitivity with respect to changes in parameter values. In this problem a parameter A_{ex} is therefore defined, that is to be estimated together with the activation energy, E, such that the rate constant is written as:

$$k = \exp(A_{ex}) \cdot \exp\left(-\frac{E}{R_g T}\right)$$

The frequency factor A is then evaluated as:

$$A = \exp(A_{ex})$$

The data indicates that the rate constant is of the order $\sim 1 \cdot 10^{-3}$ (1/s) at T = 323 K. Taking this into account and using an initial guess for the activation energy of 150 kJ/mol, an initial guess is set for A_{ex} = 49.

Reference

1. H.S. Fogler, *Elements of Chemical Reaction Engineering*, 4th ed., p. 95, Prentice Hall, 2005.

Application Library path: `Chemical_Reaction_Engineering_Module/Tutorials/activation_energy`

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 **0D**.

2 In the **Select Physics** tree, select **Chemical Species Transport>Reaction Engineering (re)**.

3 Click **Add**.

4 Click **Study**.

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

6 Click **Done**.

GLOBAL DEFINITIONS

Add a set of model parameters by importing their definitions from a data 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 `activation_energy_parameters.txt`.

Alternatively, type in the parameters directly in the **Parameters** section.

REACTION ENGINEERING (RE)

Define the parameter T_iso.

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 `T_iso`.

The reaction formula, as well as initial values for the chemical components, are added in the following way.

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 `PhN2Cl=>PhCl+N2`.

Initial Values 1

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)
PhN2Cl	`c_init_PhN2Cl`

Now, add a **Parameter Estimation** feature, define the parameters to solve for and set their initial values. For an efficient optimization procedure, also define scales for the parameters.

Parameter Estimation 1

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

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

3 In the **Parameter** table, enter the following settings:

Parameter	Initial value	Scale	Lower bound	Upper bound
Aex	49	50		

4 Click **Add**.

5 In the **Parameter** table, enter the following settings:

Parameter	Initial value	Scale	Lower bound	Upper bound
E	150e3[J/mol]	1e5[J/mol]		

Prescribing scales for the estimation parameters increases the efficiency of the optimization procedure. A good starting point is to use scales of the same order as the initial values.

Create separate **Experiment** features for the data collected at different temperatures (T_iso). Experiment nodes can be added either by right-clicking the **Parameter Estimation** node or by selecting **Experiment** from the **Reaction Engineering** toolbar, **Attributes** menu, enabled when the **Parameter Estimation** node is selected.

Experiment 1

1 In the **Reaction Engineering** toolbar, click **Attributes** and choose **Experiment**.

2 In the **Settings** window for **Experiment**, locate the **Experimental Data** section.

3 Click **Browse**.

4 Browse to the model's Application Libraries folder and double-click the file `activation_energy_experiment313K.csv`.

5 Click **Import**.

6 In the table, enter the following settings:

Data column	Use	Model variables	Unit	Weight
conc_PhN2Cl_313K	√	c_PhN2Cl	1	1

7 Locate the **Experimental Parameters** section. Click **Add**.

8 In the table, enter the following settings:

Parameter names	Parameter expressions
T_iso	313

Repeat these steps for each experiment by importing the corresponding experimental csv-file (319 K, 323 K, 328 K and 333 K) and type in the corresponding temperature in the **Experimental Parameters** table.

Before starting with the **Study**, go back to the **Reaction** node and choose settings for the reaction system.

1: PhN2Cl=>PhCl+N2

1 In the **Model Builder** window, under **Component 1 (comp1)>Reaction Engineering (re)** click **1: PhN2Cl=>PhCl+N2**.

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

3 Select the **Use Arrhenius expressions** check box.

4 In the A^f text field, type `exp(Aex)`.

5 In the E^f text field, type `E`.

Define how to solve the model.

STUDY 1

Step 1: Time Dependent

1 In the **Model Builder** window, under **Study 1** click **Step 1: Time Dependent**.

2 In the **Settings** window for **Time Dependent**, locate the **Study Settings** section.

3 In the **Output times** text field, type `range(0,50,5000)`.

Optimization

1 In the **Study** toolbar, click  **Optimization** and choose **Optimization**.

2 In the **Settings** window for **Optimization**, locate the **Optimization Solver** section.

3 From the **Method** list, choose **Levenberg-Marquardt**.

Solution 1 (sol1)

1 In the **Study** toolbar, click  **Show Default Solver**.

2 In the **Model Builder** window, expand the **Solution 1 (sol1)** node.

3 In the **Model Builder** window, expand the **Study 1>Solver Configurations>Solution 1 (sol1)>Optimization Solver 1** node, then click **Time-Dependent Solver 1**.

4 In the **Settings** window for **Time-Dependent Solver**, click to expand the **Output** section.

5 Locate the **General** section. From the **Times to store** list, choose **Output times by interpolation**.

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

The solver has now solved our model to find the kinetic parameters. In the next steps, output the estimated parameters to a table.

RESULTS

In the **Results** toolbar, click **Evaluate** and choose **Evaluate All**.

TABLE

1 Go to the **Table** window.

`E` is found to be 1.16e5 J/mol and `Aex` is evaluated to 36.9.

Perform the following steps to plot the model results and experimental data, with associated legends, as a function of time.

RESULTS

Experiment Group 313 K

1 In the **Model Builder** window, under **Results** click **Experiment 1 Group**.

2 In the **Settings** window for **1D Plot Group**, type `Experiment Group 313 K` in the **Label** text field.

3 Click to expand the **Title** section. From the **Title type** list, choose **None**.

4 Locate the **Plot Settings** section.

5 Select the **x-axis label** check box. In the associated text field, type `Time (s)`.

6 Select the **y-axis label** check box. In the associated text field, type `Concentration PhN<sub>2</sub>Cl (mol/m<sup>3</sup>)`.

7 Locate the **Legend** section. From the **Layout** list, choose **Outside graph axis area**.

8 From the **Position** list, choose **Top**.

Experiment 1 Data

1 In the **Model Builder** window, expand the **Experiment Group 313 K** node, then click **Experiment 1 Data**.

2 In the **Settings** window for **Table Graph**, click to expand the **Legends** section.

3 From the **Legends** list, choose **Manual**.

4 In the table, enter the following settings:

Legends
Experiment at 313 K

Global 1

1 In the **Model Builder** window, click **Global 1**.

2 In the **Settings** window for **Global**, locate the **Data** section.

3 From the **Parameter selection (T_iso)** list, choose **From list**.

4 In the **Parameter values (T_iso)** list, select **313**.

5 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_PhN2Cl - Concentration - mol/m³**.

6 Click **Replace Expression** in the upper-right corner of the **x-Axis Data** section. From the menu, choose **Solver>t - Time - s**.

7 Locate the **x-Axis Data** section. From the **Axis source data** list, choose **Time**.

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
Simulation at 313 K

11 In the **Experiment Group 313 K** toolbar, click **Plot**.

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

Repeat the above steps for each experiment by typing the corresponding temperature, T_iso, in the designated fields.

Optionally, delete the generated default plot.

Concentration (re)

In the **Model Builder** window, under **Results** right-click **Concentration (re)** and choose **Delete**.