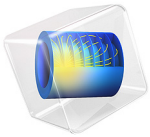


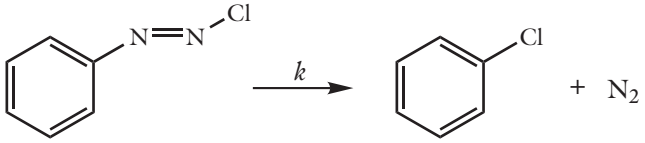
Finding Kinetic Arrhenius Parameters Using Parameter Estimation

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.

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 $A = 1.17 \cdot 10^{16}$ (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.

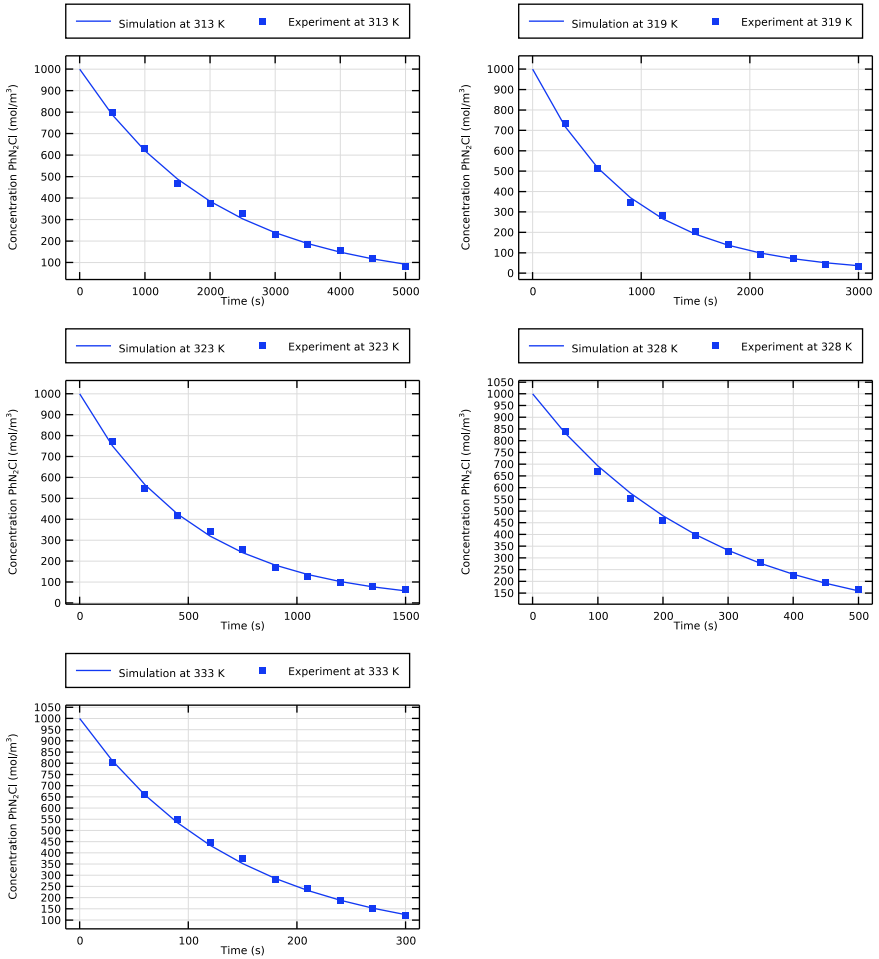


Figure 1: Model results and experimental data for PhN_2Cl concentration as a function of time.

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 and define the global least-squares objectives to be used during optimization. Add one **Global Least-Squares Objective** node for each set of experimental data available. In this tutorial model there are data from five different experiments.

COMPONENT 1 (COMP1)

Experimental data 313 K

1 In the **Model Builder** window, right-click **Component 1 (comp1)** and choose **Parameter Estimation**.

2 In the **Settings** window for **Global Least-Squares Objective**, 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 Locate the **Data Column Settings** section. In the **Model expression** text field, type `c_PhN2Cl`.

7 In the **Variable name** text field, type `c_PhN2Cl`.

8 In the **Model expression** text field, type `re.c_PhN2Cl`.

9 In the **Unit** text field, type `mol/m^3`.

10 Locate the **Experimental Conditions** section. Click **Add**.

11 In the table, enter the following settings:

Name	Expression
T_iso (Temperature)	313[K]

12 In the **Label** text field, type `Experimental data 313 K`.

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 Conditions** table.

The parameters to solve for, as well as their initial values and scales, are defined in a **Parameter Estimation** study step.

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

REACTION ENGINEERING (RE)

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`.

STUDY 1

Parameter Estimation

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

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

3 Click **Add** twice.

4 In the table, enter the following settings:

Parameter name	Initial value	Scale	Lower bound	Upper bound
Aex (Rate constant parameter)	49	49	10	100
E (Activation energy)	150e3[J/mol]	150e3[J/mol]	1e5	2e5

Use the Levenberg-Marquardt method to optimize this model.

5 Click to expand the **Output While Solving** section. Locate the **Parameter Estimation Method** section. Find the **Solver settings** subsection. From the **Least-squares time/parameter method** list, choose **Use only least-squares data points**.

Setting the **Least-squares time/parameter method** to **Use only least-squares data points** will make the time dependent solver use the times specified by the experiments.

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

The solver has now optimized the model to find the values for the kinetic parameters. The values for the optimized parameters, as well as the value for the objective function, are found in Objective Probe Table 1.

RESULTS

Objective Probe Table 1

`E` is found to be 1.16e5 J/mol and `Aex` is evaluated to 37.0.

The default plots illustrate the solution with the optimized parameter values, compared to each experimental data set used during parameter estimation. Simplify the legends and add a y-axis label.

Parameter estimation 313 K

1. In the **Model Builder** window, expand the **Results>Tables** node, then click **Results> Parameter estimation**.
2. In the **Settings** window for **1D Plot Group**, type `Parameter estimation 313 K` in the **Label** text field.
3. Locate the **Data** section. From the **Parameter selection (T_iso)** list, choose **From list**.
4. In the **Parameter values (T_iso)** list, select **313**.
5. Locate the **Plot Settings** section. In the **x-axis label** 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**.

Simulation at 313 K

1. In the **Model Builder** window, expand the **Parameter estimation 313 K** node, then click **Column 2 (model)**.
2. In the **Settings** window for **Global**, type `Simulation at 313 K` in the **Label** text field.
3. Click to expand the **Legends** section. Find the **Include** subsection. Select the **Label** check box.
4. Clear the **Solution** check box.
5. Clear the **Expression** check box.

Experiment at 313 K

1. In the **Model Builder** window, under **Results>Parameter estimation 313 K** click **Column 2 (data)**.
2. In the **Settings** window for **Global**, type `Experiment at 313 K` in the **Label** text field.
3. Locate the **Legends** section. Find the **Include** subsection. Select the **Label** check box.
4. Clear the **Solution** check box.

5 Clear the **Expression** check box.

6 In the **Parameter estimation 313 K** toolbar, click **Plot**.

Repeat the above steps for each default Parameter estimation plot.

Optionally, delete the generated default plot that was not used.

Concentration (re)

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