Ch. 5 Non-linear regression

Minimize the sum of the squares of the differences between the measured values and the calculated values for ALL the data points

Used to find the best estimates of parameter values

$$
\sigma^2 = \frac{s^2}{N - K} = \frac{1}{N - K} \sum_{i=1}^{N} \frac{(r_{im} - r_{ic})^2}{N - K}
$$

$$
s^2 = \sum (r_{im} - r_{ic})^2
$$

$N = \text{Number of runs}$

$K = \text{Number of parameters to be determined}$

$r_{im} = \text{measured reaction rate for run}$

$r_{ic} = \text{calculated reaction rate for run}$
Concentration vs. time data - batch reactor, constant volume

\[ A \rightarrow P \]

\[ -r_A = \frac{-dC_A}{dt} \]

\[ -r_A = kC_A^\alpha \]

\[ C_A^{1-\alpha} - C_A^{1-\alpha} = (1-\alpha)kt \]

\[ C_A = (C_{A0}^{1-\alpha} - (1-\alpha)kt)^{1/(1-\alpha)} \]

This expression is our calculated concentration.
What does $s^2$ look like for this?

$$s^2 = \sum_{i=1}^{N} (C_{im} - C_{ic})^2$$

We want the values for $\alpha$ and $k$ that minimize $s^2$

$$s^2 = \sum_{i=1}^{N} (C_{Aim} - C_{Aic})^2 = \sum_{i=1}^{N} \left( C_{Aim} - \left[ C_{A0}^{1-\alpha} - (1 - \alpha)kt_i \right]^{1/(1-\alpha)} \right)^2$$

In Polymath this is Rmsd$= \text{Root mean square deviation}$
We can also use time instead of concentrations

\[ C_{A0}^{1-\alpha} - C_A^{1-\alpha} = (1-\alpha)kt \]

\[ t_C = \frac{C_{A0}^{1-\alpha} - C_A^{1-\alpha}}{(1-\alpha)k} \]

\[ S^2 = \sum_{i=1}^{N} (t_{Aim} - t_{Aic})^2 = \sum_{i=1}^{N} \left[ t_{Aim} - \frac{C_{A0}^{1-\alpha} - C_{Ai}^{1-\alpha}}{(1-\alpha)k} \right]^2 \]
Let's look at problem 5-7 using nonlinear regression in polymath.

The liquid phase reaction of methanol and triphenyl takes place in a batch reactor at 25° C.

$$CH_3OH + (C_6H_5)_3CCl \rightarrow (C_6H_5)_3COCH_3 + HCl$$

For an equal molar feed the following concentration-time data was obtained for methanol:

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>$C_A$ (mol/dm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>0.278</td>
<td>0.95</td>
</tr>
<tr>
<td>1.389</td>
<td>.816</td>
</tr>
<tr>
<td>2.78</td>
<td>.707</td>
</tr>
<tr>
<td>8.33</td>
<td>.50</td>
</tr>
<tr>
<td>0.370</td>
<td>16.66</td>
</tr>
</tbody>
</table>

The following concentration-time data was carried out for an initial methanol concentration of 0.1 and an initial triphenyl concentration of 1.0.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>$C_A$ (mol/dm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>1</td>
<td>0.0847</td>
</tr>
<tr>
<td>2</td>
<td>0.0735</td>
</tr>
<tr>
<td>5</td>
<td>0.0526</td>
</tr>
<tr>
<td>10</td>
<td>0.0357</td>
</tr>
</tbody>
</table>

Find the rate law and rate law parameters.
5-7 Nonlinear regression solution

1. Postulate the rate law

\[-r_A = kC_A^\alpha C_B^\beta\]

2. Method of Excess – Data set 2 \( C_{B0} \gg C_{A0} \)

Rate law becomes

\[-r_A = k'C_A^\alpha\]

Combine w/ mole balance and integrate, solve for \( t \)

\[t_C = \frac{C_{A0}^{1-\alpha} - C_A^{1-\alpha}}{(1-\alpha)k'}\]

What do we do in polymath?

Enter experimental data
Specify the model
Enter initial guesses
Two other methods: Initial Rates, Half-Lives

Method of Initial Rates: *used when reactions are reversible*

Series of experiments carried out at different initial concentrations, $C_{A0}$, and the initial rate of reaction, $-r_{A0}$, is determined for each run.

The initial rate, $-r_{A0}$ is found by differentiating the data and extrapolating to zero time.

$$-r_{A0} = kC_{A0}^\alpha$$

<table>
<thead>
<tr>
<th>Order of Reactant</th>
<th>Change in Initial Rate when concentration is doubled</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Order</td>
<td>Rate doubles</td>
</tr>
<tr>
<td>Second Order</td>
<td>Rate quadruples</td>
</tr>
<tr>
<td>Zero Order</td>
<td>Rate remains unchanged</td>
</tr>
</tbody>
</table>
Example 5-4 Text pg. 278

Please go thru on own

\[ A \longrightarrow B + C \]

\[-r_A = kC_A^\alpha\]

<table>
<thead>
<tr>
<th>Trial</th>
<th>Conc A (M)</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01</td>
<td>4.8E-6</td>
</tr>
<tr>
<td>2</td>
<td>0.02</td>
<td>9.6E-6</td>
</tr>
<tr>
<td>3</td>
<td>0.03</td>
<td>1.4E-5</td>
</tr>
<tr>
<td>4</td>
<td>0.04</td>
<td>1.9E-5</td>
</tr>
</tbody>
</table>

\[ \ln(-ra) = 0.9864 \ln(Ca) - 7.7033 \]

\[ R^2 = 0.9997 \]
\[-r_A = k C_A^\alpha C_B^\beta\]  

Once you have \(\alpha\) and \(\beta\)  

\[k = \frac{-r_A}{C_A^\alpha C_B^\beta}\]

\[k = \frac{2.70E-7}{(0.100 \times 0.010)} = 2.7E-4\]
Method of Half-Lives

t$_{1/2}$ = time it takes for the concentration of the reactant to fall to half its initial value.

**Downfalls: requires many experiments!**

\[
A \rightarrow P
\]

\[-r_A = -\frac{dC_A}{dt}\]

\[-r_A = kC_A^\alpha\]

\[dt = kC_A^\alpha dC_A\]

Integrate the function.

Limits \(C_A = C_{A0}\) at \(t=0\)

\[
t = \frac{1}{(\alpha - 1)k} \left( \frac{1}{C_A^{\alpha-1}} - \frac{1}{C_{A0}^{\alpha-1}} \right)
\]

\[
C_A = \frac{1}{2} C_{A0}
\]

\[
t_{1/2} = \frac{1}{(\alpha - 1)k} \left( \frac{2^{\alpha-1} - 1}{C_{A0}^{\alpha-1}} \right)
\]
Do we have to use half-life? NO

\[
C_A = \frac{1}{n} C_{A0}
\]

\[
t_{1/n} = \frac{1}{(\alpha - 1)k} \left( \frac{n^{\alpha - 1} - 1}{C_{A0}^{\alpha - 1}} \right)
\]

Just like before we take natural log of both sides

\[
\ln t_{1/n} = \ln \left( \frac{1}{k} \frac{(n^{\alpha - 1} - 1)}{(\alpha - 1)} \right) + (1 - \alpha) \ln C_{A0}
\]
Classroom Exercise: 5-10, pg 298

Homework: P5-6, 5-9  
Due: Monday 3/26/07

No office hr on Tuesday, instead Wednesday 10-11 am