Solutions for R&D to Design

Guidelines for Setting Reaction Rate Constants

December 2, 2009

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Introduction

Linear plots are widely used in the case of single reactions to determine rate constants by kinetic analysis. Even in the case of composite reactions, it is possible to determine the rate constants with Excel’s solver function when the reaction equations can be integrated analytically. However, when it is impossible to analytically integrate complex reactions, this becomes a parameter estimation problem with differential equations, for which a custom modeling tool will often be used.

Regardless of whether Excel’s solver function or a custom modeling tool is used, it is very important that the initial values of the rate constants be reasonable in order to find the optimal solutions.

Here, we will introduce guidelines for determining reaction rate constants using Excel’s solver function.

Example of the Importance of Initial Values

We would like to obtain reaction rate constants from the following series reaction data and rate equations.

t [min]	0	10	30	60
A	1.0000	0.5077	0.2808	0.1385
B	0.0000	0.2808	0.4654	0.4154
C	0.0000	0.2115	0.2538	0.4462

$$A \xrightarrow{k1} B \xrightarrow{k2} C$$

$$\frac{dA}{dt} = -k_1 A$$

$$\frac{dB}{dt} = k_1 A - k_2 B$$

$$\frac{dC}{dt} = k_2 B$$

$$or, C = A_0 + B_0 + C_0 - (A+B)$$

First, analytically solve the differential equations on the left side, and then express the time-dependent change of A and B with equations.
Initial values: $A = A_0$, $B_0 = C_0 = 0$

1^{st} order linear differential equation : $\frac{dy}{dx} + P(x)y = Q(x)$

Solution : $y \cdot e^{\int Pdx} = \int e^{\int Pdx} \cdot Qdx + const.$

$$(1): \frac{dA}{dt} = -k_1 A$$

$$(2): \frac{dB}{dt} = k_1 A - k_2 B$$

$$(3): C = A_0 + B_0 + C_0 - (A+B)$$

Solution to Eq. 1: $\boxed{\frac{A}{A_0} = e^{-k_1 t}}$

Substituted in Eq. 2 :

$$\frac{dB}{dt} + k_2 B = k_1 A_0 e^{-k_1 t}$$

$$\boxed{\frac{B}{A_0} = \frac{k_1}{k_2 - k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right]}$$

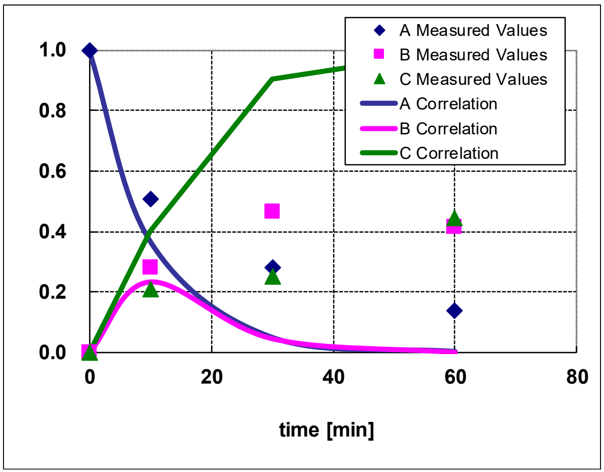
k_1 can be determined by a graph plot that becomes a straight line. However, there is no linear plot which enables determining k_2.
Therefore, we will consider determining k_1 and k_2 simultaneously with a solver.

Convergence is good with proper initial values

Before Solver

Experimental Data

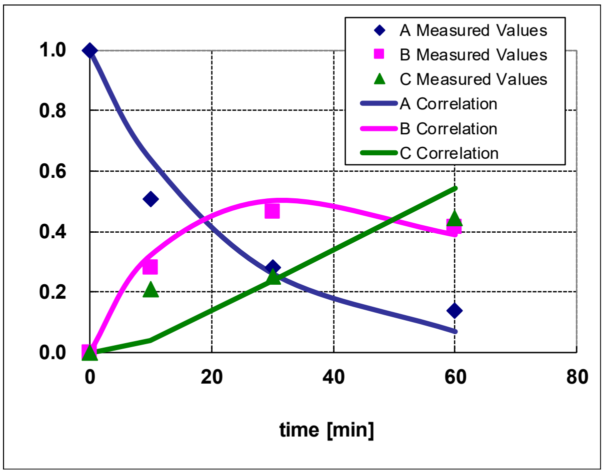
t [min]	0	10	30	60	
A	1.0000	0.5077	0.2808	0.1385	
B	0.0000	0.2808	0.4654	0.4154	
C	0.0000	0.2115	0.2538	0.4462	
k1	0.1				
k2	0.2				
A Calculated Value	1	0.36788	0.04979	0.00248	
B Calculated Value	0	0.23254	0.04731	0.00247	Total
A Squared Error	0	0.01955	0.05335	0.01849	0.09139
B Squared Error	0	0.00233	0.17479	0.1705	0.34761
C Calculated Value	0	0.39958	0.9029	0.99505	
				Sum of Squared Errors	0.439



After Solver

Experimental Data

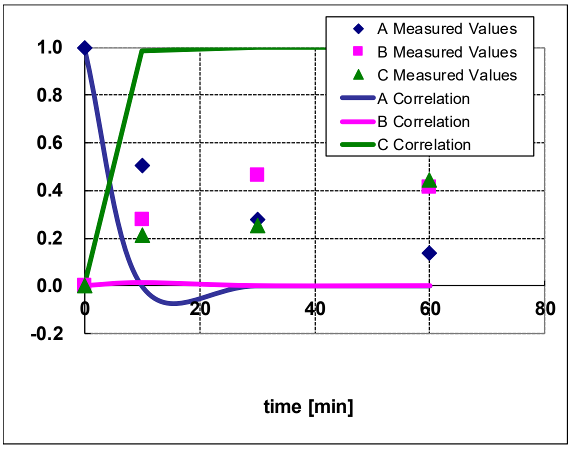
t [min]	0	10	30	60	
A	1.0000	0.5077	0.2808	0.1385	
B	0.0000	0.2808	0.4654	0.4154	
C	0.0000	0.2115	0.2538	0.4462	
k1	0.04474				
k2	0.02213				
A Calculated Value	1	0.63931	0.2613	0.06828	
B Calculated Value	0	0.3209	0.5017	0.38936	Total
A Squared Error	0	0.01732	0.00038	0.00493	0.02263
B Squared Error	0	0.00161	0.00132	0.00068	0.00361
C Calculated Value	0	0.03978	0.237	0.54237	
				Sum of Squared Errors	0.02624



Case with poor initial values that do not converge

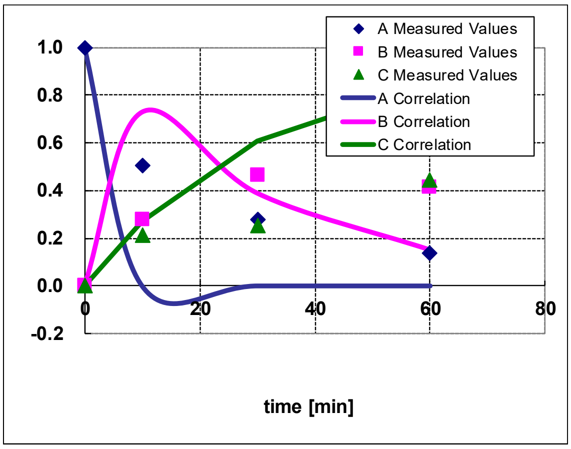
Initial Values

k1	1				
k2	0.5				
A Calculated Value	1	4.5E-05	9.4E-14	8.8E-27	
B Calculated Value	0	0.01339	6.1E-07	1.9E-13	Total
A Squared Error	0	0.25771	0.07883	0.01917	0.35571
B Squared Error	0	0.07149	0.21658	0.17254	0.46062
C Calculated Value	0	0.98657	1	1	
				Sum of Squared Errors	0.81633



Converged Values

k1	98218.2				
k2	0.03139				
A Calculated Value	1	0	0	0	
B Calculated Value	0	0.73057	0.38993	0.15205	Total
A Squared Error	0	0.25775	0.07883	0.01917	0.35575
B Squared Error	0	0.20232	0.00569	0.06935	0.27736
C Calculated Value	0	0.26943	0.61007	0.84795	
				Sum of Squared Errors	0.63312



Since the reaction rate is strongly nonlinear, it is important to choose appropriate initial values to achieve good convergence.

Guidelines for Setting Rate Constants

We would like to obtain reaction rate constants from the following sequential reaction data and rate equations.

t [min]	0	10	30	60
A	1.0000	0.5077	0.2808	0.1385
B	0.0000	0.2808	0.4654	0.4154
C	0.0000	0.2115	0.2538	0.4462

$$A \xrightarrow{k1} B \xrightarrow{k2} C$$

$$\frac{dA}{dt} = -k_1 A$$

$$\frac{dB}{dt} = k_1 A - k_2 B$$

$$\frac{dC}{dt} = k_2 B$$

$$or, C = A_0 + B_0 + C_0 - (A + B)$$

$$\frac{dA}{dt} = -k_1 A$$

$$\frac{dB}{dt} = k_1 A - k_2 B$$

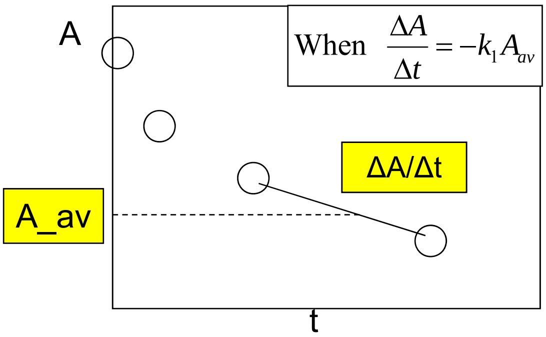
$$\frac{dC}{dt} = k_2 B$$

The derivative is approximated by a linear change using a small time difference, and the concentration term is approximated by an average value.

$$\left(\frac{\Delta A}{\Delta t}\right) = -k_1 A_{av}$$

$$\left(\frac{\Delta B}{\Delta t}\right) = k_1 A_{av} - k_2 B_{av}$$

$$\left(\frac{\Delta C}{\Delta t}\right) = k_2 B_{av}$$



When $\frac{\Delta A}{\Delta t} = -k_1 A_{av}$

k_1 can be calculated directly as k_1= -(ΔA /Δt)/A_{av} , but as the number of reactions increases, it is necessary to solve simultaneous equations for estimating the rate constants. However, since these equations are linear, they can be solved easily by the Excel solver.

Calculate $\Delta A/\Delta t$, A_{av} (average concentration) and the like

⇩

Assume k_1=1.0, k_2=0.5

⇩

Using k_1, k_2 calculate $(\Delta A/\Delta t)_{cal}$ (= $-k_1 \times A_{av}^2$) and the like

⇩

Calculate k_1 and k_2 with the Excel solver so as to minimize the error of $(\Delta A/\Delta t)$, $(\Delta A/\Delta t)_{cal}$ and the like.

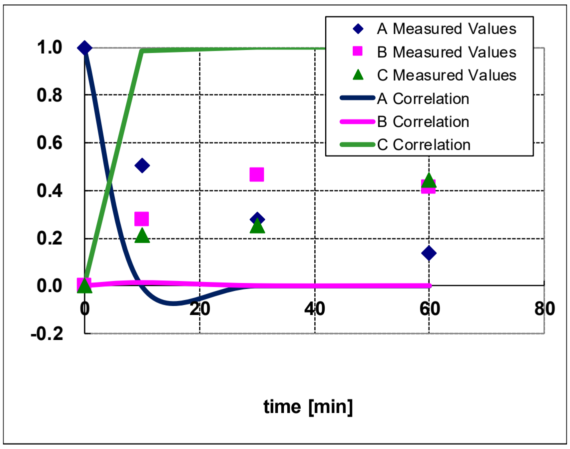
Before Solver

Experimental Data

t [min]	0	10	30	60
A	1.0000	0.5077	0.2808	0.1385
B	0.0000	0.2808	0.4654	0.4154
C	0.0000	0.2115	0.2538	0.4462

Calculation for estimation

tav	5	20	45	
Aav	0.753846	0.394231	0.209615	
Bav	0.140385	0.373077	0.440385	
Cav	0.105769	0.232692	0.35	
Left Side ΔA/Δt	-0.049231	-0.01135	-0.00474	
Left Side ΔB/Δt	0.028077	0.009231	-0.00167	
Left Side ΔC/Δt	0.021154	0.002115	0.00641	
k1=	1			
k2=	0.5			
Right Side ΔA/Δt=-k1*Aav	-0.753846	-0.39423	-0.20962	
Right Side ΔB/Δt=k1*Aav-k2*Bav	0.683654	0.207692	-0.01058	
Right Side ΔC/Δt=k2*Bav	0.070192	0.186538	0.220192	
Squared Errors				
ΔA/Δt	0.496483	0.146601	0.041972	
ΔB/Δt	0.429781	0.039387	7.94E-05	
ΔC/Δt	0.002405	0.034012	0.045703	
total	0.928669	0.219999	0.087755	1.236423



Simulation with estimated values

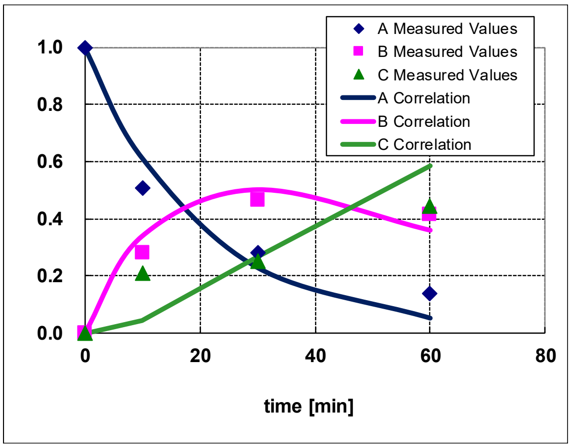
k1	1			
k2	0.5			
A Calculated Value	1	4.54E-05	9.36E-14	8.76E-27
B Calculated Value	0	0.013385	6.12E-07	1.87E-13
C Calculated Value	0	0.98657	0.999999	1

After Solver

The method for estimating the rate constants as the solutions of linear equations obtained by converting differential equations into difference equations is effective for providing the initial values of the subsequent optimization calculation.

Calculation for estimation

tav	5	20	45	
Aav	0.753846	0.394231	0.209615	
Bav	0.140385	0.373077	0.440385	
Cav	0.105769	0.232692	0.35	
Left Side ΔA/Δt	-0.049231	-0.01135	-0.00474	
Left Side ΔB/Δt	0.028077	0.009231	-0.00167	
Left Side ΔC/Δt	0.021154	0.002115	0.00641	
k1=	0.049034			
k2=	0.02389			
Right Side ΔA/Δt=-k1*Aav	-0.036964	-0.01933	-0.01028	
Right Side ΔB/Δt=k1*Aav-k2*Bav	0.033611	0.010418	-0.00024	
Right Side ΔC/Δt=k2*Bav	0.003354	0.008913	0.010521	
Squared Errors				
ΔA/Δt	0.00015	6.38E-05	3.06E-05	
ΔB/Δt	3.06E-05	1.41E-06	2.03E-06	
ΔC/Δt	0.000317	4.62E-05	1.69E-05	
total	0.000498	0.000111	4.96E-05	0.000659



Conclusion

- To approximate reaction rate constants, transform differential equations into difference equations. The linear simultaneous equations obtained by this method can be easily solved by Excel.
- It is possible to efficiently determine the rate constants by optimizing these approximate results as initial values with a custom modeling tool or the like.
- When attempting to simultaneously determine Arrhenius parameters (activation energy and frequency factor) from reaction data having different temperatures in particular, the order of parameters is completely different, so convergence is often difficult. Even in such a case, it is possible to obtain reasonable approximate values of activation energies and frequency factors by estimating the reaction rates in advance at each temperature and drawing Arrhenius plots.