A Pseudo-Order Kinetic Analysis

The file "Pseudo-Order Data" contains kinetic data for the reaction

$$\mathrm{R_1 + R_2 + R_3 \rightarrow products}$$

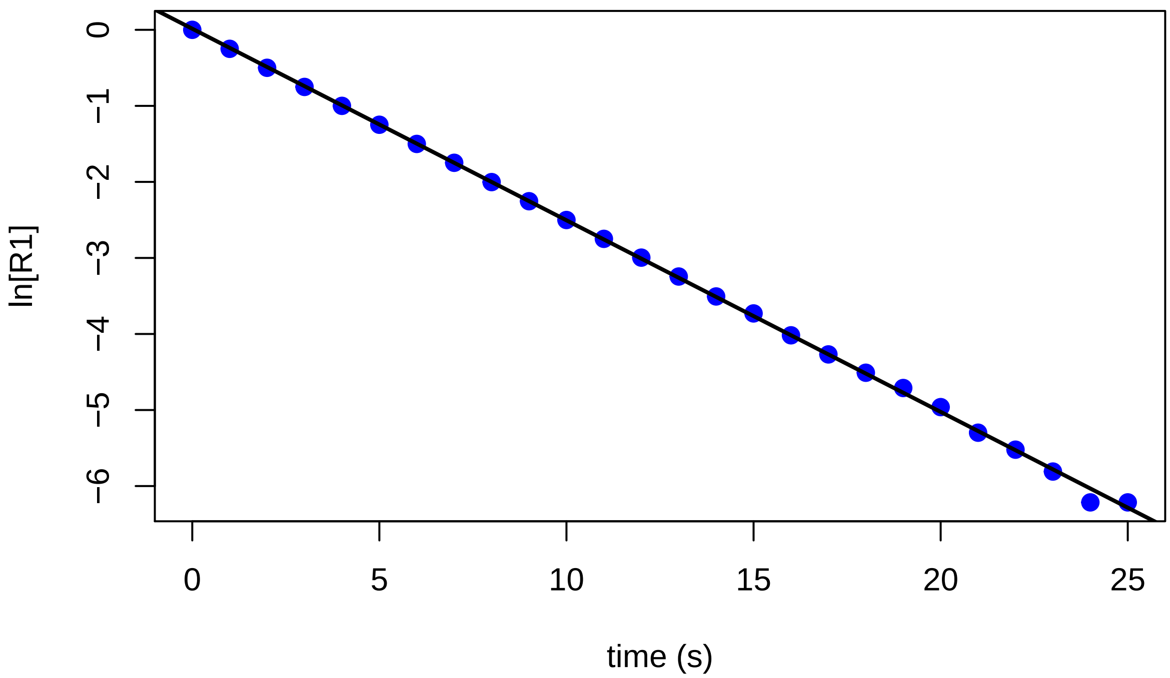
Each page contains data for a pseudo-order experiment in which the concentration of one reactant is significantly smaller than the concentration of the other two reactants. Using this data, determine the reaction's order with respect to each reactant, the three pseudo-order rate constants, the reaction's overall rate constant, and the overall rate law.

Answer

The rate law for the reaction is of the general form

$$R = k[\mathrm{R_1}]^{\alpha}[\mathrm{R_2}]^{\beta}[\mathrm{R_3}]^{\gamma}$$

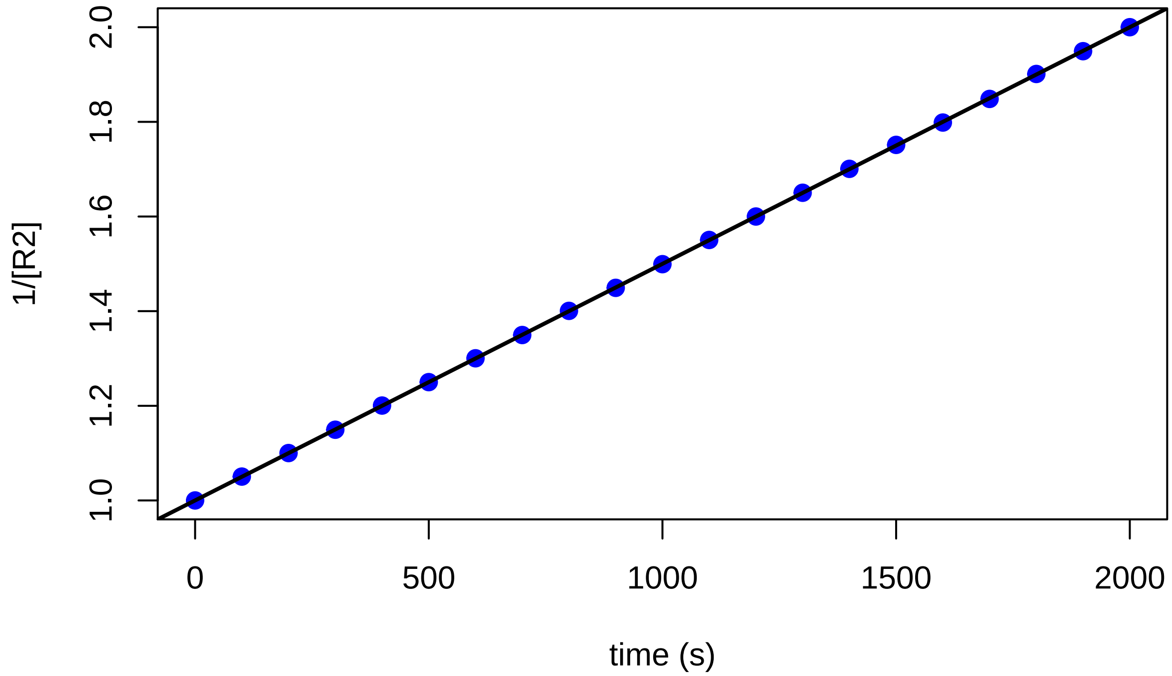
The data on the first page shows first-order kinetics because a plot $\ln[\mathrm{R_1}]$ vs. time, as shown here, is a straight-line; thus, we know that α is 1.



Fitting a straight-line to the data give a slope of –0.250 s^{-1}, which means that the observed rate constant is

$$(k_{obs})_1 = k[\mathrm{R_2}]^{\beta}[\mathrm{R_3}]^{\gamma} = 0.250 \text{ s}^{-1}$$

The data on the second page shows second-order kinetics because a plot $[\mathrm{R_2}]^{-1}$ vs. time, as shown here (and plotting every 100th point for clarity), is a straight-line; thus, we know that β is 2.

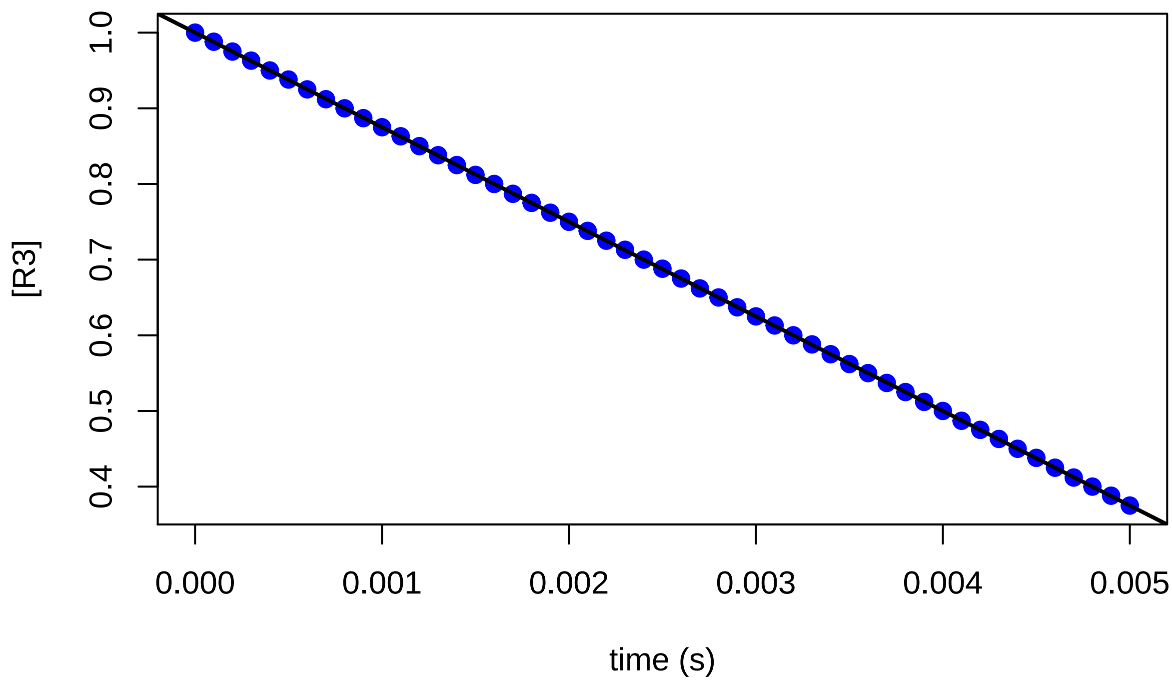


Fitting a straight-line to the data give a slope of -5.00×10^{-4} $\text{mM}^{-1}\text{s}^{-1}$, which means that the observed rate constant is

$$(k_{obs})_2 = k[\text{R}_1][\text{R}_3]^\gamma = 5.00 \times 10^{-4}\ \text{mM}^{-1}\text{s}^{-1}$$

where we already know that α is 1.

The data on the third page shows zero-order kinetics because a plot $[\text{R}_3]$ vs. time, as shown here, is a straight-line; thus, we know that γ is 0.



Fitting a straight-line to the data give a slope of –125 mM/s, which means that the observed rate constant is

$$(k_{obs})_3 = k[\mathrm{R}_1][\mathrm{R}_2]^2 = 125 \text{ mM/s}$$

where we already know that α is 1 and that β is 2.

The reaction's rate law is

$$R = k[\mathrm{R}_1][\mathrm{R}_2]^2$$

To find the rate constant, k, we solve each of the expressions for (k_{obs}) using the known concentrations for R_1 and for R_2; thus

$$(k_{obs})_1 = k[\mathrm{R}_2]^\beta[\mathrm{R}_3]^\gamma = k[500 \text{ mM}]^2[500 \text{ mM}]^0 = 0.250 \text{ s}^{-1}$$

which gives $k = 1.0 \times 10^{-6} \text{ mM}^{-2}\text{s}^{-1}$. The same approach with the other two observed rate constants (left to you to verify), yields the same value for k.