Processes Kinetics Modeling: A Numerical Study

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Introduction

The kinetics study of the reaction between Cu\textsuperscript{2+} and S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} in solutions is not entirely studied, being reported into the specialty literature just few papers which refer the reaction in aqueous solutions.

Aim

By using of a set of experimental data obtained from stopped flow spectrophotometrical installation build at Technical University of Cluj-Napoca, to investigate the kinetic of the reaction.

Assumption

The general form of the reaction is $A + B \leftrightarrow X \rightarrow P$

Experimental procedure

The cooper and tiosulfate aqueous solutions were prepared in different concentrations varying from 0.001 M to 0.01 M.

The reaction was detected to be a very fast one: the existence of the X intermediary was found to be below 25 ms.

The wavelength of light detection diode was found (and is 430 nm) in order to prepare the detection of intermediary forming as the wavelength which assures the best stability of the light emission in time.

A microampere meter was set in order to be used for recording of the signal from detector and the baud rate of the recording was choused to be 0.04 ms.

A digital oscilloscope with buffer was used to plot and transfer the data to the computer.

In order to minimize the experimental interferences such as dilution of the intermediary, the size of the mixing chamber was varied; a small size one was selected and used for measurements. The mixing chamber has a volume equal to 0.35 cm\textsuperscript{3} and the length of optical pathway traversed by the beam through measurement chamber is 0.4 cm.

Experiments
Three experiments with equal concentration of reactants (0.001, 0.005 and 0.01 M) are the subject of this investigation.

The recording of digital data was started always after the mixing moment but near to, because of limited memory buffer of the oscilloscope (64 Kb).

The number of relevant measurements corresponding to the reaction time it varies in 1500-8000 range.

**Mathematical Methods**

The Lambert-Beer law was used to correlate extinction with concentration; the unknown parameter was the molar extinction coefficient. The mathematical model of the assumed reaction mechanism was numerically written; the unknown parameters were four partial reaction orders and three reaction rates constants.

The subject of optimization was squared sum of differences between experimental extinction E and theoretical approach of extinction a[X]. Only a first part of the experimental data records entered into the optimization procedure (1100 for 0.001 M, 1300 for 0.005 M, and 6500 for 0.01M).

**Results**

The optimization procedure produced the best fit of the model to the experiment with 0.962, 0.955, and 0.980 respectively correlation coefficients.

Not all unknown parameters were possible to be obtained. Reaction rates: only to the right ones. Partial orders: all, except one of intermediary for the left direction reaction. Extinction coefficient: 212 +/- 22 l/mol*cm. For all obtained parameters is no significant difference between parameters values from one experiment to another with a 95% confidence.

**Conclusion**

Reaction kinetics was almost complete determined. Reaction rates: 2000 +/- 1000, N/A, 2200 +/- 200, partial orders: 0.789 +/- 0.05, 0.781 +/- 0.04, N/A, 1.55 +/- 0.04.

The optimization procedure was proved to be a self consistent one, despite of the number of unknown parameters used.

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Thanks for providing the experimental data to Dr. Mihaela Ligia UNGUREȘAN from Technical University of Cluj-Napoca, Romania.
Experimental Data

The results of the optimized variables and constants for partial reaction orders \( y_0, y_1, y_2, y_3 \), reaction rate constants \( k_0, k_1, k_2, k_3 \), and for the minimization function \( S_{\text{min}} \) are presented in Table 1. Graphical representations of the variation of optimized parameters for experiment number 1 (from five to five iterations) are presented in Figure 1-8.

Method

Assumption: The general form of the investigated reaction is

\[ A + B \rightarrow \text{产物} \]

and the associated reaction rates are:

\[ \nu = k_1[A]^3[B]^2; \nu = k_2[X]^4; \nu = k_3[X]^4 \]

where \([A], [B],\) and \([X]\) are the concentrations of chemicals at a moment of reaction, \( k_1 (1, 2, 3) \) are the reaction rate constants, and \( y_i (i = 1, \ldots, 4) \) are partial reaction orders.

Mathematical Methods

The Lambert-Beer law was used to correlate extinction with concentration; the unknown parameter was the molar extinction coefficient, \( E = \varepsilon \cdot l \cdot C \), where \( \varepsilon \) = molar extinction coefficient, \( E \) = estimated extinction by the model, \( X \) = intermediaries concentrations.

The mathematical model of the assumed reaction mechanism was developed; the unknown parameters were four partial reaction orders and three reaction rate constants.

The optimum was considered in case in which the method was convergent towards credible results, and the optimized values of variables become almost constant. Following criteria were imposed: (1) valid reaction rates; (2) the values of constants used in model belonging to the 95% confidence intervals; and (3) lower values for the variation of constant values used in optimization.

Because the reaction between copper (II) ions and tiosulfate ions is a very fast one, the first part of the experimental data were included in optimization procedure: (1) 1100 determinations for the reaction at 0.001 M, (2) 1200 determinations for the reaction at 0.005 M, and (3) 6500 determinations for the reaction at 0.01M.

Results

The variances of the regression coefficients \((a, b)\) for each experiment, reported to the iteration are in Figure 9 and 10, respectively. The plot of the experimental determination versus time and the optimized values by the model for iteration cycle of 1003 is presented in Figure 11.

Table 1. The values of the optimized parameters

<table>
<thead>
<tr>
<th>Experiment</th>
<th>( y_0 )</th>
<th>( y_1 )</th>
<th>( y_2 )</th>
<th>( y_3 )</th>
<th>( k_0 )</th>
<th>( k_1 )</th>
<th>( k_2 )</th>
<th>( k_3 )</th>
<th>( S_{\text{min}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.No 1</td>
<td>1.509</td>
<td>0.823</td>
<td>0.807</td>
<td>0.745</td>
<td>3.46·10^3</td>
<td>1.02·10^3</td>
<td>8.20·10^2</td>
<td>N.R.</td>
<td>1.81·10^-5</td>
</tr>
<tr>
<td>Exp.No 3</td>
<td>1.571</td>
<td>0.799</td>
<td>0.791</td>
<td>0.745</td>
<td>2.30·10^3</td>
<td>2.04·10^3</td>
<td>2.10·10^3</td>
<td>N.R.</td>
<td>5.82·10^-3</td>
</tr>
<tr>
<td>Exp.No 4</td>
<td>1.571</td>
<td>1.622</td>
<td>1.601</td>
<td>1.571</td>
<td>2.30·10^3</td>
<td>2.04·10^3</td>
<td>2.10·10^3</td>
<td>N.R.</td>
<td>1.81·10^-5</td>
</tr>
</tbody>
</table>

Table 2. Statistical characteristics of the regression equations

<table>
<thead>
<tr>
<th>Experiment</th>
<th>( a )</th>
<th>( b )</th>
<th>( r )</th>
<th>( S_{\text{min}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.No 1</td>
<td>0.18</td>
<td>2.07</td>
<td>0.96</td>
<td>1.81·10^-5</td>
</tr>
<tr>
<td>Exp.No 2</td>
<td>0.09</td>
<td>2.07</td>
<td>0.95</td>
<td>6.66·10^-4</td>
</tr>
<tr>
<td>Exp.No 3</td>
<td>0.18</td>
<td>2.07</td>
<td>0.99</td>
<td>5.82·10^-3</td>
</tr>
</tbody>
</table>

Conclusion

Reaction kinetics was almost complete determined. Reaction rates: 2000 +/- 1000, N/A, 2200 +/- 200, partial orders: 0.789 +/- 0.05, 0.781 +/- 0.4, N/A, 1.55 +/- 0.04.

Despite of the number of unknown parameters used, the proposed optimization procedure proved to be self-consistent.

Acknowledgements

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References

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Experimental: Cu$^{2+}$ and S$_2$O$_3^{2-}$

- The cooper and tiosulfate aqueous solutions prepared in different equal concentrations varying from 0.001 M to 0.01 M (0.001 M – Exp.No.1, 0.005 M – Exp.No.2, and 0.01 M – Exp.No.3) were the subject of this investigation. The reaction was detected to be a very fast one: the existence of the X intermediary was found to be below 25 ms.

- The wavelength of light detection diode was found (and is 430 nm) in order to prepare the detection of intermediary forming as the wavelength which assures the best stability of the light emission in time.

- A microampere meter was set in order to be used for recording of the signal from detector and the baud rate of the recording was chose to be 0.04 ms.

- A digital oscilloscope with buffer was used to plot and transfer the data to the computer.

- The number of relevant measurements corresponding to the reaction time varied between 1500 and 8000 range.
Model: $A + B \xrightleftharpoons[\frac{k_2}{k_1}]^{k_1} X \xrightarrow[k_3]{\;} P$

- and the associated reaction rates are: $\nu = k_1[A]^{y_1}[B]^{y_2}$; $\nu = k_2[X]^{y_3}$; $\nu = k_3[X]^{y_4}$, where $[A]$, $[B]$, and $[X]$ are the concentration of chemicals at a moment of reaction, $k_j$ ($j = 1, 2, 3$) are the reaction rates constants, and $y_i$ ($i = 1, \ldots, 4$) are partial reaction orders.

- The Lambert-Beer law was used to correlate extinction with concentration; the unknown parameter was the molar extinction coefficient: $\varepsilon = \frac{\bar{E}}{I \cdot X}$, where $\varepsilon = \text{molar extinction coefficient}$, $\bar{E}$ = estimated extinction by the model, $X =$ intermediary concentrations

Results – next slide
Reaction kinetics was **almost complete determined**. Reaction rates: $k_1=2000 +/- 1000$, $k_2=N/A$, $k_3=2200 +/- 200$, partial orders: $y_1=0.789 +/- 0.05$, $y_2=0.781 +/- 0.04$, $y_3=N/A$, $y_4=1.55 +/- 0.04$. Despite of the number of unknown parameters used, the proposed optimization procedure proved to be self-consistent.
Acknowledgements

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• Thanks for providing the experimental data for this study to Mihaela L. UNGUREȘAN from Technical University of Cluj-Napoca, Romania (ET108 project member).
• Thank you for your attention
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