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# MODEL FORMULATION AND INTERPRETATION –
# FROM EXPERIMENT TO THEORY

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**Abstract:** From kinetics study of a given pair of reactants different types of mechanisms were investigated. A mathematical model was formulated. Model parameters were evaluated and assessed. Obtained results from the optimization procedure opened an interesting discussion about the limits of experiments parameters for imposed conditions, such as mechanism type and collecting procedure. By using of a least squares method were obtained models as best fits correlates (results shown an average of 96.6%) with experimental measurements. Comparison between experiments shown that the obtained model is a consistent one, all obtained parameters being in the same range of 95% confidence interval. These results validate experimental as well as from model data.

## 1. Introduction

Kinetic-based methods are used in determination of various substances, as chlo-

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rine and oxychlorine species [1], GPT activity in human serum [2], silver traces [3], interaction between Cu(II) and Fe(II) ions [4] by the use of flow-injection analysis [5] or continuous-flow operations [6]. First study of reaction between $Cu[NH_3]_4^{2}+$ and $S_2O_3^{2-}$ was reported in 1973 by Byerley et. al. [7]. Almost twenty years later, Rabai and Epstein published results regarding kinetics of interaction between $Cu^{2+}$ with $S_2O_3^{2-}$ in aqueous solution [8]. A stopped-flow installation for study the kinetic of fast reactions was been built and used for the reaction between tiosulfate and copper ions [9]. Starting with a previous experience in optimization of processes [10], an optimization procedure has been developed for kinetics reaction between tiosulfate and copper ions and their consistency are discussed here.

## 2. Material and Method

### 2.1. Experimental Data

The cooper and tiosulfate aqueous solutions were prepared in different concentrations varying from 0.001 M to 0.01 M. The reaction is very fast; there were observed that the X intermediary products appear below 25 ms from starting point. The wavelength of light detection diode used into the experiments was selected to be 430 nm (assuring the best stability of the light emission in time). A microampere metter recorded the signal from detector with 0.04 ms baud rate. A digital oscilloscope with buffer was used to plot and transfer the data to a computer. In order to minimize the experimental interferences, such as dilution of the intermediary, a small size chamber was selected and used in experiments. The mixing chamber was of 0.35 cm$^3$; the length of optical pathway traversed by the beam through measurement chamber was of 0.4 cm. Three experiments with equal concentration of reactants (0.001, 0.005, and 0.01 M respectively) were conducted and are discussed here. The recording of digital data was started always after the mixing moment, but very close to, having limited oscilloscope buffer memory (64 Kb). Relevant measurements corresponding to the reaction times varied from 1500 to 8000.

## 2.2. Mathematical Model

Let us take into consideration the reaction between two chemicals A and B with the following form:

$$A + B \rightleftharpoons_{k_2}^{k_1} X \rightarrow^{k_3} P, \ v_1 = k_1[A]^{y_0}[B]^{y_1}; v_2 = k_2[X]^{y_2}; v_3 = k_3[X]^{y_3} \quad (1)$$
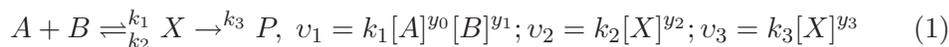
where [A], [B], and [X] are instantaneous concentrations, $v_j$ $(j = \overline{0..2})$ rates, $k_j$ $(j = \overline{0..2})$ rates constants, and $y_j$ $(j = \overline{0..3})$ partial orders. Differencing:

$$d[A] = -k_0[A]^{y_0}[B]^{y_1}dt + k_1X^{y_2}dt; \ d[B] = -k_0[A]^{y_0}[B]^{y_1}dt + k_1[X]^{y_2}dt,$$

$$d[X] = (k_0[A]^{y_0}[B]^{y_1} - k_1[X]^{y_2} - k_2[X]^{y_3})dt. \quad (2)$$

The expression of chemicals concentrations can be iterated as in equation (3), where $y_0, y_1, y_2, y_3$ partial reaction orders:

$$D_{i-1} = k_0 A_{i-1}^{y_0} B_{i-1}^{y_1} dt - k_1 X_{i-1}^{y_2} dt,$$

$$A_i = A_{i-1} - D_i; \ B_i = B_{i-1} - D_i; \ X_i = X_{i-1} + D_{i-1} - k_2 X_{i-1}^{y_3}. \quad (3)$$

## 2.3. Optimization Procedure

The optimization procedure starts from the following conditions: $X_0 = 0$ mol/l (intermediary product of reaction initial concentration); $A_0 = B_0$ (initial concentrations of the reactants); $dt = 4 \cdot 10^{-5}$s (the detector baud rate); $N$ measurements (depends on experiment, vary from 1100 to 6500). Followings are subject to optimization: reaction rate constants ($k_0$, $k_1$, $k_2$), partial reaction orders ($y_0$, $y_1$, $y_2$, $y_3$), molar extinction coefficient $\varepsilon$ ($a = \varepsilon \cdot l$, a being the regression slope from estimated extinction ($\hat{E}$) regression equation (see eq 4). The aim of the optimization procedure was to obtain values of above mentioned parameters through successive iterations.

$$\hat{E} = a \cdot [X], \ \hat{E} \text{ estimator of experimental extinction } E. \quad (4)$$

## 2.4. Working Methodology

The principles of the optimization procedure were: For given values of ($k_j$, $j = \overline{0..2}$) and ($y_j$, $j = \overline{0..3}$) the series of intermediary concentration X are obtained iterative X = X(n). The extinction values E = E(n), obtained from experiments and the intermediary concentrations X = X(n) obtained from kinetic modeling constitutes a series of N pairs (X, E); Having N pairs (X, E) a quality factor function called S can be defined depending on X and E values; S vary depending on choosed rates constants and partial reaction orders: S = S($k_0$, ..., $k_2$, $y_0$,

..., $y_3$). The aim was minimizing of S function. One of the main problems was to define the S function; thus, a series of S expressions were tried. The expression anticipated by the equation (4) was proved to produce consistent result in optimization. Thus S were calculated using formula (where M is the arithmetic mean function):

$$S = M(E^2) + M^2([X]E) - 2M^2([X]E)/M([X]^2).\qquad(5)$$

Let diff be a small relative variation (diff was set to 1%); for each variable ($k_0$, ..., $k_2$, $y_0$, ..., $y_3$) a small relative variation was made (for $k_1$: $0.99 \cdot k_1$, $1.00 \cdot k_1$, $1.01 \cdot k_1$). When all variables vary, a number of $3^7$ different series of values were obtained; for each series, the quality factor S was calculated. Algorithm advances on iterating based on the minimum of quality factor S selected from all $3^7$ values computed at one iteration. The optimum process was considered when the method convergenced towards credible results, and the optimized values of variable become almost constant. Following criteria were imposed: minimum residual error S; valid reaction rates (nonnegative, acceptable range); the model parameters values fits one to each other to 95% confidence intervals for all three experimental data sets; lower values for the variation of constant values used in optimization. Note that the reaction between copper (II) and tiosulfate ions is very fast, measurements being difficult to do. Only the first part of the experimental data were relevant and entered into the optimization procedure (1100 for 0.001 M, 1300 for 0.005 M, and 6500 for 0.01M).

## 3. Results and Discussion

Obtained results are in Table 1, where $a$ and $b$ are coefficients of the regression equation $\hat{E} = aX + b$. The dependence of the regression coefficients $a$ and $b$, correlation coefficient $r$ and residues sum $S$ depending on iteration step are in Figure 1. As in Figure 1, the $a$ coefficient stabilized at positive values starting with iteration 27 for 1-st and 3-rd experiment and with iteration 28 for 2-nd experiment. The coefficient $b$ had positive values till iteration 17 (1-st), 11 (2-nd) and 8 (3-rd), taking negative values after; stabilizes at iteration 26 for 1-st, and 20 for 2-nd and 3-rd; stabilization at negative value could be explained by the errors in measurements (had not any physical and/or chemical significance, it is just as resulted from the experiment). Note that the values of $b$ vary insignificant (for example, for step 10, vary less than $7.8 \cdot 10^{-3}$). The correlation coefficient stabilizes at iteration 23 for 1-st, and at 18 for 2-nd and 3-rd experiments. Above the stabilization point, the variances of the

| E | $y_0$ | $y_1$ | $y_3$ | $k_0$ | $k_2$ | $S$ | $C_0$ | $a$ | $b$ | $r$ | $IS$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.82 | 0.81 | 1.51 | 3.46 | 2.30 | 1.81 | 1 | 219 | -0.0005 | 0.980 | 107 |
| 2 | 0.80 | 0.79 | 1.57 | 1.02 | 2.04 | 66.6 | 5 | 189 | -0.0821 | 0.955 | 99 |
| 3 | 0.75 | 0.75 | 1.57 | 0.82 | 2.10 | 582 | 10 | 227 | -0.1300 | 0.962 | 99 |

E - experiment no; $y_0$ to $y_3$ - partial orders; $k_0$, $k_2$ - rates ($\cdot 10^3$); $y_2$, $k_1$ - not reliable; S - residue ($\cdot 10^{-5}$); $\hat{E}$ = aX+b; r - correlation coefficient; IS = Iteration Step; $C_0 = [A_0]=[B_0]$ (mMoles)

Table 1: Optimized parameters values and its statistics

correlation coefficients were insignificant. The optimized objective function $S$ stabilizes around the iteration 15 for 1-st and 2-nd and 17 for 3-rd. There can be considered that the optimization method was stabilized at the iteration equal with 28. After the iteration equal with 28, the variance of the $r$ coefficient, the $a$ and $b$ coefficients, and $S$ objective function were not significant.

The results of optimized variables and constants for partial reaction orders, reaction rate constants, and for the objective function are also in Table 1. The proposed optimization process was able to optimized three out of four partial reaction orders and two out of three reaction constants. The partial reaction order $y_2$ took values between 1 and 2 without bringing to the model significant changes in terms of correlation with experimental determinations. More, the values of the partial reaction order $y_2$ were considered as not reliable because did not had any stabilization tendency (its values increased with iteration, comparing with the values of the other partial reaction orders - $y_0$, $y_1$, and $y_3$ which stabilized starting with iteration 24 for 1-st, and with 17 for 2-nd and 3-rd). It can be said that the partial reaction orders obtained through optimization are reliable and for all three experiments the optimized values are around 1.5 (see $y_3$ in the table). The value of the partial reaction orders can derive from a reaction order of 2 or of 1.5 (more reliable of 1.5), but in no case not exceed the value equal with 2. It can be observed that the results obtained for 1-st experiment (when the reactants concentrations were $10^{-3}$M) are close to the experiment (see the correlation coefficient between extinction values from optimization and calculated based on experimental data). Looking at the convergence of the optimization methods and at the stabilization of the coefficients, 1-st experiment is most reliable (in terms of data quality and results) and 3-rd experiment is most compromised. The plots for 1-st experiment of the experimental extinction versus time and the optimized values for iteration cycles 107, 86, 65, 44, 23, and 2 versus time (being all overlapped) are in Figure 2. Note
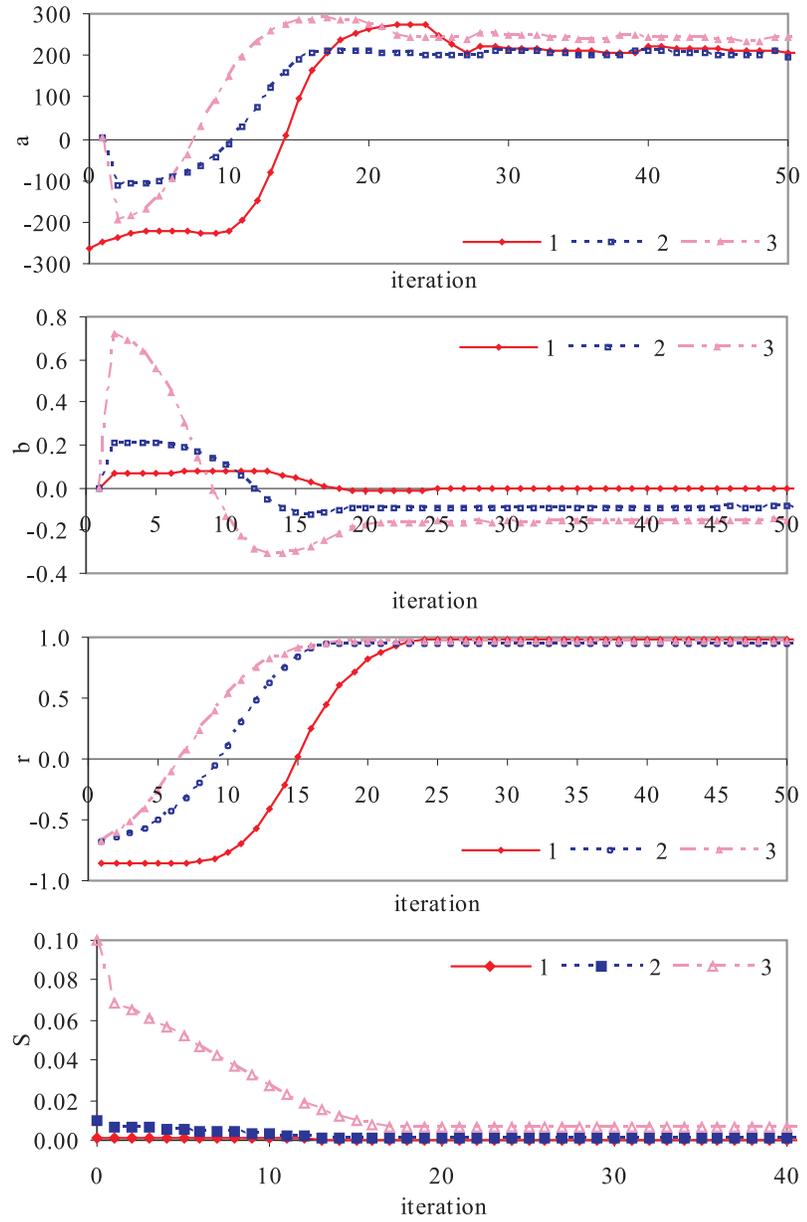
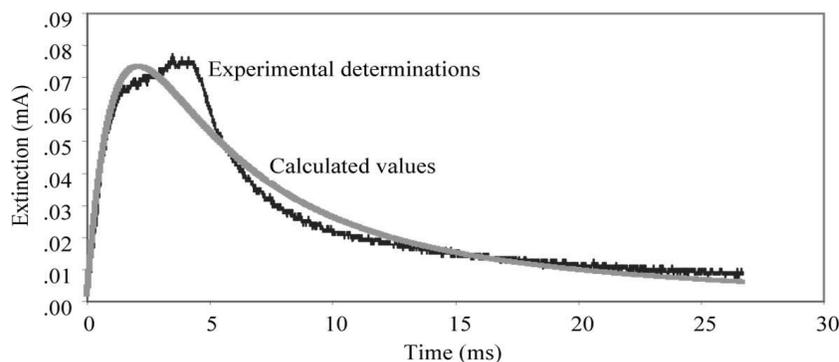Figure 1: $a$, $b$, $r$, and $S$ versus iteration for all three data sets

Figure 2: $S$ residue versus iteration for all three data sets

that, the obtained values are not identical; they are just much closed to each other and could not be identified separately on the graphic. Overlapping of the optimization results obtained for different iteration steps sustain the stability and reliability of the optimization model.

## 4. Conclusions

The obtained results are far to be perfect; But proposed optimization method is converging towards credible results for the reaction: partial orders and rates into error limits, credible variance of the constants. The certainties are the values of the partial orders, rates and constants, values that stabilized with iteration. Neither the proposed method of calculus nor experimental determinations were rigorous. Note that, being a fast reaction, biases can appear easy in collecting of the experimental determinations. The proposed mathematical model proved to be rapid and versatile optimization method.

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