Kinetics of Electron Transfer Reaction Between Co(II) and Chlorate Ions: Isothermal Reactor Design and Experimental Validation

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Summary: The Batch Stirred Tank Reactor (BSTR) has been commonly used for decades in the chemical process industries and even on a pilot plant or laboratory scale whenever expensive and delicate raw materials and products such as pharmaceuticals or fragile transition metal complexes are involved. This research article describes the details of isothermal BSTR and subsequent experimental validation of the rate law discovered in the previous paper of this series on the electron transfer reaction between Co(II) and chlorate ions in acetic acid solution. A Series of tests were performed to evaluate the efficiency of the BSTR at multiple temperatures and illustrate the differences between the theoretical and experimental conversion of potassium chlorate through relative error. The experimental conversions are calculated with the design equation. Theoretical and experimental conversions are correlated and proportional to the initial concentrations of the reactant and electron transfer reaction among the reactants. Based on the parameters of the design equation, a set with average parameters was chosen and tested over BSTR. The model was then validated for different temperatures and conversions. A design equation for the BSTR has been written and applied for the conversions of 25%, 50%, 75%, and 95%. The time interval is going to be predicted by the model to achieve the desired conversions. The percent relative error between predicted and experimental conversions clearly shows the model's predictability, power, and reliability. The precision of the observed rate constant for the electron transfer reaction is found to be 2.2023×10^{-2} %.

Introduction

A kinetic model was developed for the electron transfer reaction between Cobalt(II) and chlorate ions in glacial acetic acid. It consists of treating the acetic acid solution of cobalt(II) acetate tetrahydrate with aqueous potassium chlorate according to the following ionic reaction:

$$\left[ClO_3^- + 6H^+ + 6Co(II) \xrightarrow{H_2O,\ 85-90^\circ C,\ \approx 15min} 6Co(III) + Cl^- + 3H_2O\right]$$
(1)
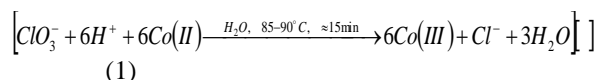
It was reported by [1,2] that the oxidative conversion of Co(II) to Co(III) using chlorate as an oxidizing agent in acetic acid solution follows a rate law that is first order in chlorate concentration but has a fractional order ($0.7455 \approx \frac{3}{4}$) for Co(II). The rate law took the following form,

$$r = k\, C_A C_B^{0.7455} \qquad (2)$$

Here C_A and C_B are concentrations of potassium chlorate and cobalt(II) acetate, respectively. In terms of C_P concentration of Co(III) alone:

$$\frac{dC_P}{dt} = 6A\exp\left(\frac{-E}{RT}\right)\left(C_{A_0} - \frac{C_P}{6}\right)\left(C_{B_0} - C_P\right)^{0.7455}$$
(3)

Here C_{Ao} and C_{Bo} are initial concentrations of potassium chlorate and cobalt(II) acetate, respectively.

Equation (2) was developed based on an extensive set of kinetic data collected for varying conditions, for the temperature and the initial concentrations of reactants. The model rate law was then analyzed for its predictive power against the same experimental data provided by [1]. Although the rate law's precision was excellent, there was a need to validate the model under new sets of conditions. This research article describes the details of the isothermal batch stirred tank reactor design and subsequent original experimental validation of the rate law discovered during our earlier study on the electron transfer reaction between Co(II) and chlorate ions in acetic acid solution.

For the validation of rate law (3), the design equations for an isothermal, constant-volume BSTR could be used. The rate law can be used to compute time for some theoretical conversion, and the reactor is operated to achieve the experimental conversion. The relative error comparison is calculated by comparing theoretical and experimental conversions to know the precision of the theoretical model [4-6].

BSTR Design

BSTR can be accurately operated for extremely mild reaction conditions, providing exceptional control over process variables and the quality of the product [7,8]. The only drawbacks are its relatively small capacity for processing [9] and manual to semi-automatic process control [10], as compared to the large-scale automatic flow reactors [11-12]. Nevertheless, high-purity fine chemicals, e.g., homogeneous catalysts, are usually produced on a limited scale. In such cases, the limited size of BSTR and its strict control over mild process variables becomes a blessing as it requires much less capital investment [13-14]. The standard design procedure for BSTR is given in several textbooks on chemical reaction engineering [15-16].

BSTR design of reaction system

Rate law (3) for reaction system may conversely be written in terms of observed rate constant k and order of reaction α, β.

$$\frac{dC_P}{dt} = k\left(C_{A_0} - \frac{C_P}{6}\right)^\alpha \left(C_{B_0} - C_P\right)^\beta \qquad (4)$$

This equation may be expressed in terms of the concentration of chlorate using the equation

$$C_{A_0}\frac{dx_A}{dt} = k\left[C_{A_0}\left(1 - x_A\right)\right]^\alpha \left[C_{B_0} - 6C_{A_0}x_A\right]^\beta$$

(5)

the conversion of   A (x_A) is defined as

$$x_A = \frac{C_{A_0} - C_A}{C_{A_0}}$$

It is the required design equation for an isothermal, constant-volume BSTR for chlorate conversion. The solution of the differential equation (5) is a given in equation (6)

$$t_{Cal} = C_{B_0}\int_0^{x_B} \frac{dx_B}{6k\left[C_{A_0} - \frac{C_{B_0}x_B}{6}\right]^\alpha \left[C_{B_0}\left(1 - x_B\right)\right]^\beta}$$

(6)

where conversion of B (xB) is defined as

$$x_B = \frac{C_{B_0} - C_B}{C_{B_0}}$$

Equation (6) will give the required theoretical computed time t_{Cal} for a certain theoretical fractional conversion of chlorate within the BSTR. Analytical solutions to equations (6), is not possible. The Adaptive Quadrature algorithm can be useful for functions that change rapidly over an interval such as the conversion of either chlorate or Co(II) in the time domain that increases rapidly during initial stages of the reaction. The Mathcad was used to implement the algorithm.

The equation (6) would hardly ever have an integer value of the computed time. Therefore, the computed time t_{Exp} in seconds was rounded off to the nearest integer to run the reactor. The corresponding round-off error incorporated can be eliminated by using the following equation for the calculation of corrected experimental conversion:

$$x_{A_{Exp}} = \left(1 - \frac{t_{Exp} - t_{Cal}}{t_{Cal}}\right)\left(\frac{C_{A_0} - C_A}{C_{A_0}}\right) \quad (7)$$

Equation (7) is used during experimental validation of the rate law for the oxidative conversion of Co(II) to Co(III) using chlorate as an oxidizing agent in acetic acid solution.

Experimental

Based on the advanced reaction technique, it was found that the simplest option for a low-cost isothermal, constant volume reactor design involves a batch reactor system with a jacketed glass vessel. A Series of tests were performed to evaluate the efficiency of the batch reactor at multiple temperatures. The experimental rig and procedures were described in the article [1]. Exception, during the validation, runs at the optimized conditions and consists of the allowance of higher time for reducing Co(III) ions, especially in reaction mixtures for the second configuration, which was increased from 10 to 15 minutes. This modification was necessary because the reaction mixture in the second configuration contains a relatively higher Co(III) concentration during the entire experimental time domain that naturally requires additional time for a complete reduction before being analyzed biamperometrically. All the results presented herein were obtained on an Intel Core Duo-based personal computer (HP 520 Notebook) using Mathcad Professional (MathSoft, Inc.) and Microsoft Excel (Microsoft Corporation).
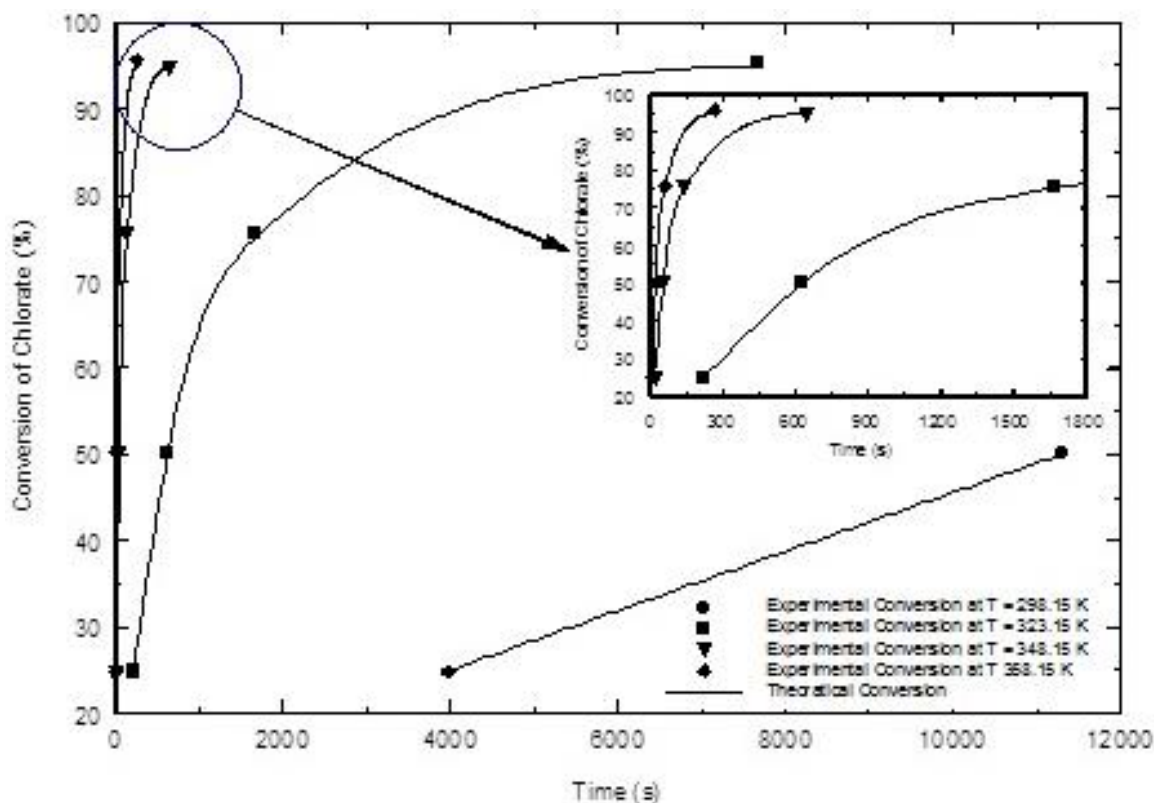
Fig 1**:** BSTR model validation: Conversion of Chlorate vs Time.

Results and Discussion

Theoretical isotherms for constant volume BSTR design of reaction

The processing times t_{Cal} for various theoretical fractional conversions (0, 25, 50, 75 and 95%) and temperatures (25º, 50º, 75º and 85ºC) were computed by solving equation (6) numerically using the Adaptive-Runge-Kutta algorithm between $t_{Cal} = 0 \rightarrow 12000$ ----- with the initial value being $x_A(0) =$

Fig 1 Represents the graphical validation of the BSTR model. The results of numerical integration and the solutions of equation (6) and zoom can be seen in Fig 1 in the form of isotherms. It shows the plot of chlorate conversion against time for different temperatures such as 298 K, 323 K, 343 K, and 353 K. The operation of BSTR at 25ºC would not be an economical choice; for example, at 25% theoretical conversion, t_{Cal} is slightly more than an hour and becomes more than 38 hours for 95% conversion. Hence at 298, the conversion was tested only for 25%

and 50%. However, at higher temperatures, 75 and 95% conversions were also tested and compared with the corresponding theoretical conversion; a reasonable relative error of ± 1.19% was found. Reduction of practical considerations starts from 50ºC as for 25% conversion at this temperature, t_{Cal} is less than 4 minutes, equivalent to 94.46% reduction t_{Cal} with 50% increase in temperature. Further reductions in t_{Cal} the temperature rise are not that significant, e.g., for 25% conversion at 75ºC and 85ºC, the reduction in times t_{Cal} are 5.07% and 0.28%, respectively, for 33.33% and 11.76% increase in temperatures. An exactly similar trend can be noticed for higher conversions [17].

The theoretical response of BSTR for the reaction system has been summarized in Fig 2. For lower conversions, BSTR must be operated at lower temperatures and for higher conversions at a higher temperature. The corresponding practical values for processing time ($10 \min < t_{Cal} < 30 \min$) for BSTR operation.
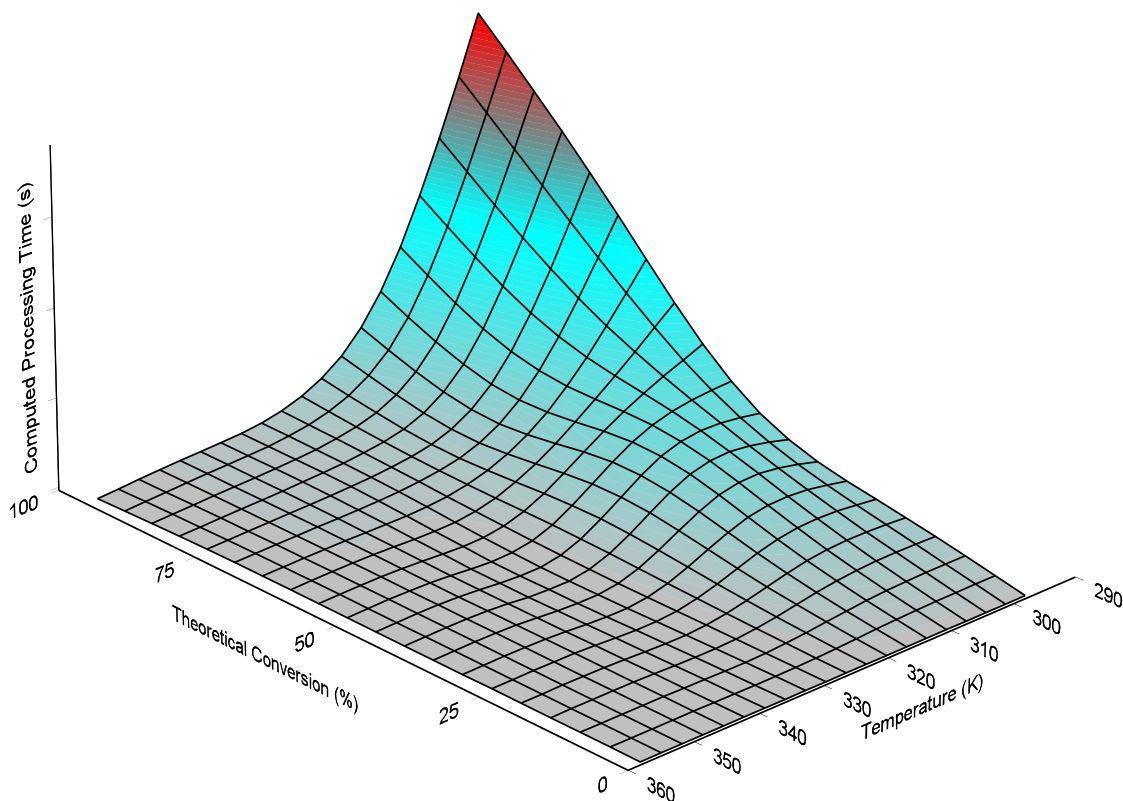
Fig 2: Theoretical response of BSTR for reaction system.

Validation of Proposed Kinetic Model

Experiments were then performed using the same laboratory reactor rig for various theoretical conversions (0, 25, 50, 75, and 95%) and temperatures (25°, 50°, 75°, and 85°C). The results of the validation experiments are contained in Table 1 – 4, in Fig 3, and zoom in Fig 4. For comparison, the solutions of equation (6) for the same experimental conditions are plotted in Figs 3 – 4; as can be seen, the corrected experimental conversions $x_{A_{Exp}}$ wonderfully follow the same footprints as do the solutions of equation (6). The relative errors between theoretical and corrected experimental conversions are exceptionally low ($-1.2 < RE < 1$), which is a strong sign of the appropriateness of the proposed kinetic model.

Fig 5 exhibits an incomparable linear fit between theoretical and corrected experimental conversions and R^2 is indeed almost unity which is a sign of perfect fit. Although there is virtually no variation for low – moderate conversions, for higher conversion (95%) there is inconsequential variation in

the points. It may be attributed to the fact that the rate law (equation 2) excellently describes the kinetic behavior of the reaction system in the early–middle stages. As the reaction proceeds and products accumulate, the reactants deplete in the reactor. The predictive capability of the rate law decreases because of the interference caused by the products [18]. The residuals follow the normal distribution (Fig 6) with a mean value of 0.1580% and a standard deviation of 0.3648%. There is a fair balance in the random nature of the residuals, with positive deviations slightly greater than negative ones.

For the validation of kinetic model which is developed in previous paper. A design equation for the BSTR has been written and applied for the conversions of 25%, 50%, 75%, and 95%. The time interval is going to be predicted by the model to achieve the desired conversions. Table 1 - 4 shows corrected experimental conversions. The percent relative error between predicted and experimental conversions in the table shows the model's predictability, power, and reliability determine the operational strategy for a.

Table-1: BSTR model validation for 25% conversion.

Processing Temperature (K)	Predicted Processing Time (s)	Volume of 23 mM Na₂S₂O₃ Consumed (mL)	Corrected Experimental Conversion (%)	Relative error (%)
298.15	3995	1.24	24.81	-0.77
323.15	221	1.24	24.83	-0.67
348.15	19	1.26	24.70	-1.19
358.15	8	1.30	24.76	-0.96

Table-2: BSTR model validation for 50% conversion.

Processing Temperature (K)	Predicted Processing Time (s)	Volume of 23 mM Na₂S₂O₃ Consumed (mL)	Corrected Experimental Conversion (%)	Relative error (%)
298.15	11298	2.50	50.02	0.04
323.15	626	2.50	49.99	-0.02
348.15	53	2.52	50.11	0.22
358.15	22	2.56	50.25	0.49

Table-3: BSTR model validation for 75% conversion.

Processing Temperature (K)	Predicted Processing Time (s)	Volume of 23 mM Na₂S₂O₃ Consumed (mL)	Corrected Experimental Conversion (%)	Relative error (%)
298.15	30230	--	--	--
323.15	1674	3.78	75.63	0.84
348.15	141	3.78	75.61	0.80
358.15	58	3.80	75.72	0.96

Table-4: BSTR model validation for 95% conversion.

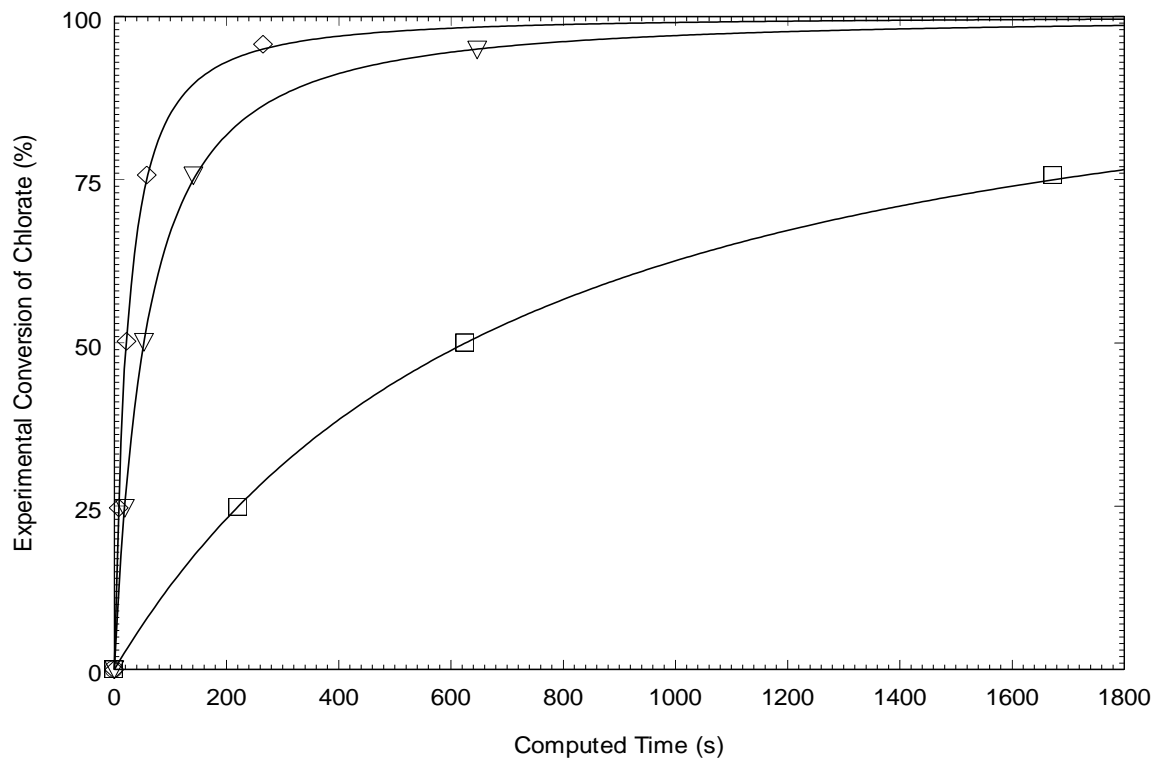| Processing Temperature (K)	Predicted Processing Time (s)	Volume of 23 mM Na₂S₂O₃ Consumed (mL)	Corrected Experimental Conversion (%)	Relative error (%)
298.15	138781	--	--	--
323.15	7685	4.76	95.24	0.26
348.15	647	4.74	94.85	-0.15
358.15	265	4.78	95.71	0.74

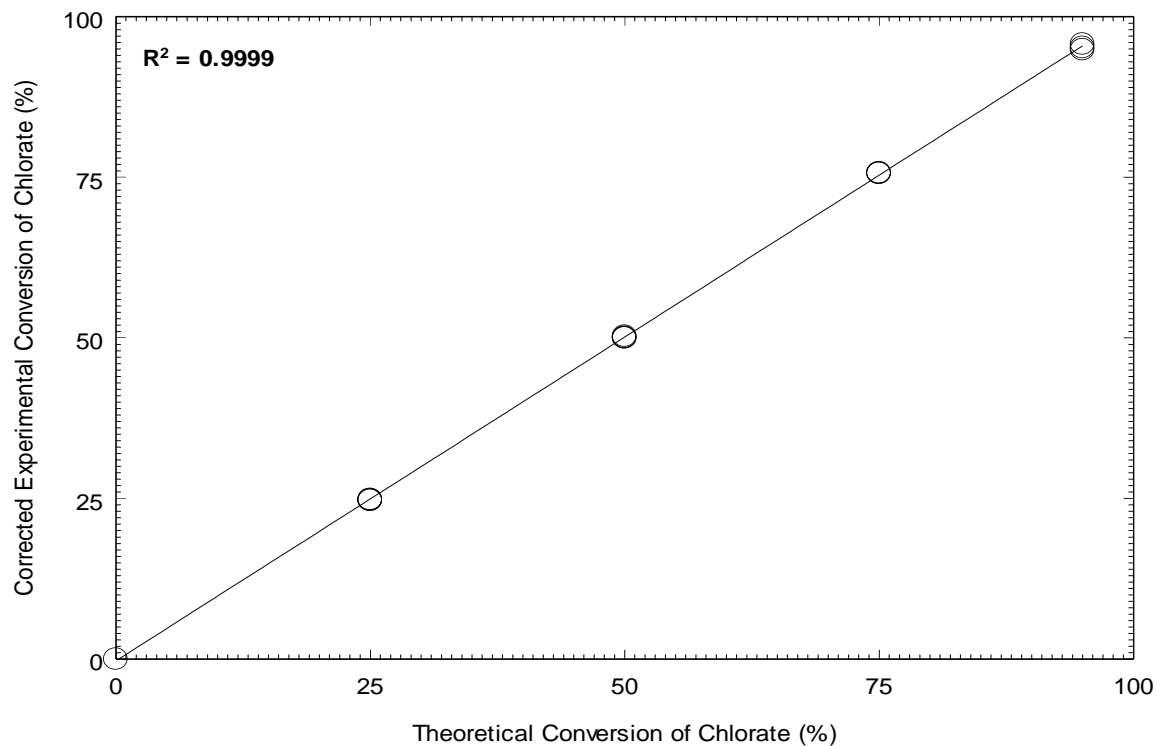Fig 4**:** Zoom view of Fig 3.

Fig 5:   Linear fit between theoretical and corrected experimental conversions of Chlorate for Proposed KM validation.
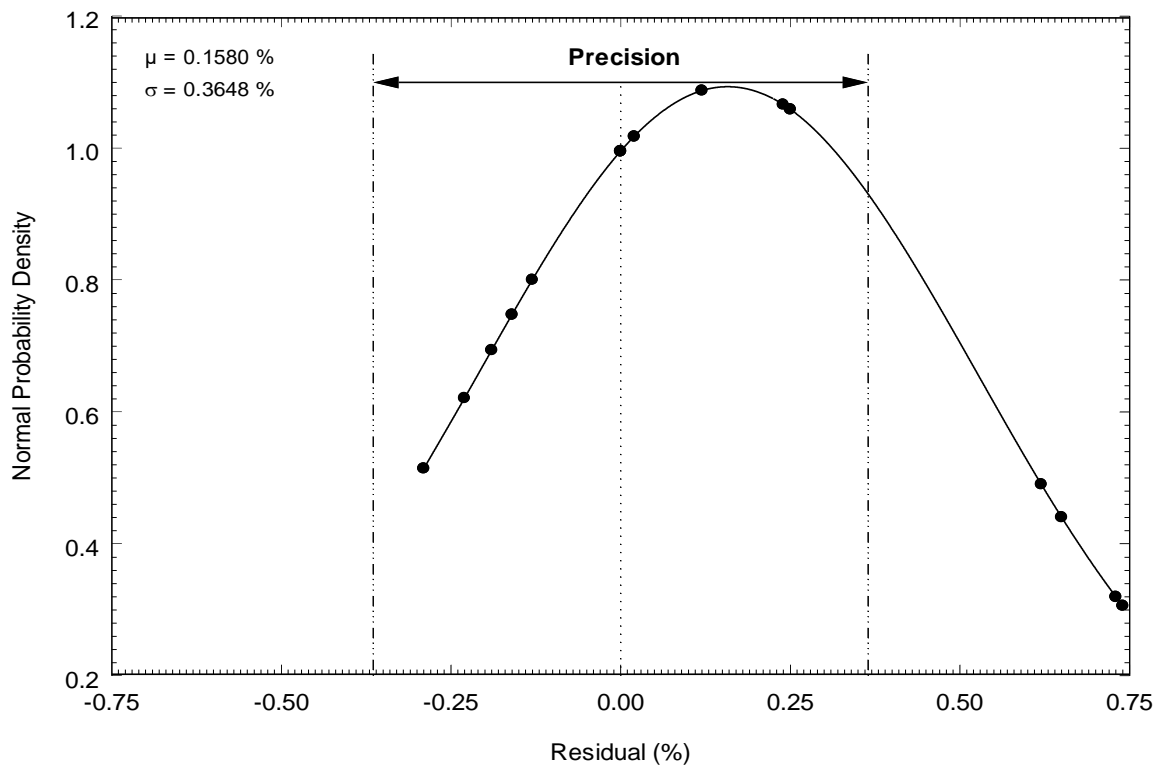

Fig. 6:   Residual analysis for linear fit in Fig 4: mean value μ, standard deviation σ.

Rate Law And Precision Of Estimated Rate Constant

In the light of the previous discussion, the rate of the reaction system may be best described by the following rate law:

$$r = 6kC_A C_B^{0.7455}$$

By rearrangement and taking logarithms:

$$ln6k = lnr - lnC_A - 0.7455lnC_B \qquad (8)$$

In this relation the dependent variable is k and independent variables are r, C_A and C_B all of which are experimental quantities. The observed rate constant k is indirectly estimated from the estimated values of Arrhenius equation parameters [1]. The precision values for both r and C_P are known. Since C_A and C_B are functions of C_P, the precision of C_A and C_B will be equal to that of C_P. With this information in hand the fractional error or precision of the observed rate constant k of the reaction system may be defined as (Hill 2014; Smith 1970):

$$\left(\frac{\Delta k}{k}\right)^2 = \left(\frac{\partial \ln k}{\partial \ln r}\right)^2\left(\frac{\Delta r}{r}\right)^2 + \left(\frac{\partial \ln k}{\partial \ln C_A}\right)^2\left(\frac{\Delta C_A}{C_A}\right)^2 + \left(\frac{\partial \ln k}{\partial \ln C_B}\right)^2\left(\frac{\Delta C_B}{C_B}\right)^2 \qquad (9)$$

The squares of the partial derivatives in equation (9) are derived from the partial differentiation of equation (8):

$$\left(\frac{\partial \ln k}{\partial \ln r}\right)^2 = \left(\frac{\partial \ln k}{\partial \ln C_A}\right)^2 = 1 \qquad (10)$$

$$\left(\frac{\partial \ln k}{\partial \ln C_B}\right)^2 = 0.7455^2 \qquad (11)$$

The fractional errors in C_P and r have been estimated in [1] and are given below:

$$\frac{\Delta r}{r} = 1.594 \times 10^{-5}, \ \frac{\Delta C_P}{C_P} = \frac{\Delta C_A}{C_A} = \frac{\Delta C_B}{C_B} = 1.761 \times 10^{-4}, \ \frac{\Delta k}{k} = 2.2023 \times 10^{-4}$$

Conclusion

This study successfully validated the rate law for the electron transfer reaction between Co(II) and chlorate ions for isothermal BSTR. The kinetic model predicted the desired conversion of reactants would be achieved within time. This result shows that the observed rate constants for the reaction system have an extremely remarkable precision of 2.2023×10^{-2} %. This highly precise nature of the rate constants is reflected in the validation experiments summary in Fig (5). The rate law may be used for every practical purpose, such as to design a BSTR for an industrial, pilot plant, or laboratory scale operation.

Acknowledgement

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