

To: Dr. Marat Orazov

From: Group 6 (Just Diene) - Daniel Robinson, Abdul Fayed, Neel Shah, Evan Sciacchitano

Subject: KIN Phase II Update - Memo Report

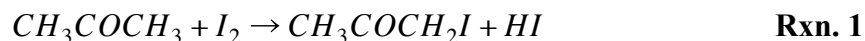
Date: May 2nd, 2021

AGENDA

1. Introduction and Background (Evan)
 - a. Define the problem and state relevant parameters
2. Data Analysis
 - a. Determining the Overall Rate Order and Arrhenius Pre-Exponential Factor (Dan)
 - b. Experimental runs for determining of the Overall Rate Order (Abdul)
 - c. Error Analysis: confidence intervals, error propagation, and interpretation (Dan)
3. Phase III Planning (Neel)
 - a. Assign teamwork and conduct sensitivity analysis
 - b. Model a batch reactor and CSTR
 - c. Prepare and revise the final report (Everyone)

INTRODUCTION

In this experiment, the analysis on iodination of acetone experiment was carried out in MATLAB and Excel to determine the reaction order and Arrhenius parameters from the simulated data. The overall reaction is as shown below in **Rxn. 1**.



The reaction is acid catalyzed, where the acid used was hydrochloric acid (HCl). A proposed general reaction order was determined to be zero order in I_2 and first order in both acetone and HCl, yet, thorough simulated data analysis has to be performed to obtain the true reaction order. The rate law for the reaction could be generalized below in **Eq. 1**.

$$Rate = k[Acetone]^\alpha [HCl]^\beta [I_2]^\gamma \quad \text{Eq. 1}$$

The Arrhenius relationship could be used to determine the activation energy, E_a and pre-exponential factor, A of the reaction. The relationship is as shown below in **Eq. 2**.

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad \text{Eq. 2}$$

14 different runs were prepared to obtain the simulated I_2 absorbance data in MATLAB by using the p-code provided. The conditions for each run are summarized in **Table 1** below.

Table 1: Different Starting Conditions for Each Run for Data Simulation

| Run | Temperature (°C) | [Acetone] ₀ (M) | [HCl] ₀ (M) | [I ₂] ₀ (M) | Time (s) |
|-----|------------------|----------------------------|------------------------|------------------------------------|----------|
| 1 | 35 | 2 | 0.02 | 0.0020 | 180 |
| 2 | 35 | 1 | 0.02 | 0.0020 | 180 |
| 3 | 35 | 3 | 0.02 | 0.0020 | 180 |
| 4 | 35 | 4 | 0.02 | 0.0020 | 180 |
| 5 | 35 | 2 | 0.01 | 0.0020 | 180 |
| 6 | 35 | 2 | 0.03 | 0.0020 | 180 |
| 7 | 35 | 2 | 0.04 | 0.0020 | 180 |
| 8 | 35 | 2 | 0.02 | 0.0010 | 180 |
| 9 | 35 | 2 | 0.02 | 0.0030 | 180 |
| 10 | 35 | 2 | 0.02 | 0.0040 | 180 |
| 11 | 30 | 2 | 0.02 | 0.0020 | 180 |
| 12 | 33 | 2 | 0.02 | 0.0020 | 180 |
| 13 | 40 | 2 | 0.02 | 0.0020 | 180 |
| 14 | 38 | 2 | 0.02 | 0.0020 | 180 |

From **Table 1**, Run 1 is regarded as the standard condition, where the rest of the runs are only varied by one parameter at a time while remaining the rest constant. **Run 2 - 10** are temperature independent, where they only vary by the concentration of reactants. **Run 2 - 4**, **Run 5 - 7**, and **Run 8 - 10** are when the acetone, HCl, and I₂ concentrations are varied respectively. **Run 11 - 14** are temperature dependent, where the temperatures are varied from the standard conditions, which play a role in determining the E_a and A of reaction.

RESULTS AND DISCUSSIONS

Absorbance data of I₂ for each run can be obtained from running the p-code provided in MATLAB. The absorbance data was then linearized by using the given calibration line equation to obtain the concentration of I₂, as shown in **Eq. 3**.

$$\text{Absorbance} = 96.654[I_2] + 0.0476 \quad \text{Eq. 3}$$

Concentration of I₂ is then plotted against the time to perform initial rate method analysis. Only approximately 1-10% of the first few data points were used to calculate the initial rate of reaction to ensure that it truly reflected the initial rate. By using all runs, the order with respect to each reactant was obtained by performing multiple linear regression at once in Excel by using **Eq. 4**, which is a linearized form of **Eq. 1**. The order and respective errors are as tabulated in **Table 2**.

$$\ln r_0 = \ln k + \alpha \ln[\text{Acetone}] + \beta \ln[\text{HCl}] + \gamma \ln[I_2] \quad \text{Eq. 4}$$

Table 2: Reaction Orders with Errors

| Parameter | Value ($\pm 95\%$ C.I.) | Standard Error | P-value |
|-----------|--------------------------|----------------|---------|
| α | 0.9876 ± 0.5771 | 0.0210 | 0.0034 |
| β | 1.0014 ± 0.5771 | 0.0191 | 0.0031 |
| γ | -0.0003 ± 0.5771 | -0.0001 | 0.9990 |

The values of α and β are significant since the p-value is greater than 0.05, whereas γ is insignificant with high p-value. From the order with respect to each reactant and the initial reaction rate, the rate constant k could be determined, by considering only the last 4 runs (**Runs 11 - 14**), where the temperature varies. A and E_a were determined by linearizing **Eq. 2**, as shown in **Eq. 5**, and the values are as tabulated in **Table 3**.

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \quad \text{Eq. 5}$$

Table 3: Activation Energy and Pre-exponential Factor Values with Confidence Interval

| Parameter | Values | 95% Confidence Interval | P-value |
|------------------------------------|------------------------|--|---------|
| A ($\text{M}^{-1}\text{s}^{-1}$) | 1.026×10^{11} | $5.951 \times 10^8 - 1.769 \times 10^{13}$ | 0.0006 |
| E_a (kJ/mol) | 83.0101 | 69.8104 - 96.2098 | 0.0003 |

Figure 1 shows the plot of **Eq. 5** with all 5 data points of **Run 11 - 14**, with the error bars of each $\ln k$ value and the 95% confidence interval band.

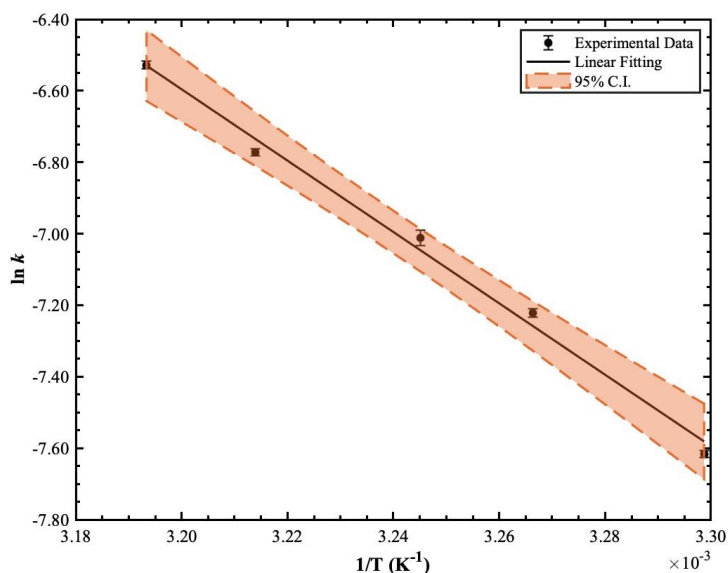


Figure 1: 95% confidence interval band for Arrhenius equation linearization for Run 11 - 14 data points.

Error was propagated throughout the entire analysis with the error sources being mass, temperature, absorbance, and the slope and intercept from regressions. The error from the above sources leads to error in the rate orders for the three chemicals, the activation energy, the pre exponential factor, and the rate constant. This error propagation is dictated by the below equations where **Eq. 6** is for addition, **Eq. 7** is for multiplication and division, and **Eq. 8** is for exponentials.

$$\sigma_x = \sqrt{\sigma_a^2 + \sigma_b^2 + \sigma_c^2} \quad \text{Eq. 6}$$

$$\frac{\sigma_x}{x} = \sqrt{\frac{\sigma_a^2}{a^2} + \frac{\sigma_b^2}{b^2} + \frac{\sigma_c^2}{c^2}} \quad \text{Eq. 7}$$

$$\frac{\sigma_x}{x} = y\left(\frac{\sigma_a}{a}\right) \quad \text{Eq. 8}$$

Then based upon the associated error for the above parameters a 95% confidence interval can be calculated using the following **Eq. 9**. Excel functions were used to calculate the t-values and p-values required to conduct this analysis.

$$\text{Conf. Interval} = SE \text{ in } Y \text{ for each } X \cdot \sqrt{\frac{1 + (x - \bar{x})^2}{n \sum \sigma^2}} \quad \text{Eq. 9}$$

FUTURE PLANS

In order to obtain better results for this experiment, a different set of initial conditions must be used. Start by looking at the error that is included by the various measurements taken in the experimental procedure. Examples of measuring devices are the mass scale, graduated cylinder, thermocouple, etc. However, random variation and error has been built into the p-code that was run to determine the absorbance of iodine over time, thus each time the code is run slightly different results are generated. It should be noted that when running the actual physical lab, error would likely have been much greater due to the associated systematic error.

To prepare for phase 3 and gain familiarity with Aspen Plus, the tutorial on Canvas should be followed. However, it became apparent that all three parts can be completed in MATLAB except for the sensitivity analysis which will be done through Aspen.

Kinetics Lab (KIN)

Phase II Presentation

Group Name: Just Diene (Group 6)

Instructor: Dr. Marat Orazov

Date: May 2nd, 2021

Group Members:

Daniel Robinson

Abdul Fayed

Neel Shah

Evan Sciacchitano



AGENDA

- Introduction (Evan) ~ 2 minutes
- Data Analysis ~ 10 minutes
 - Error Propagation (Dan)
 - Rate Orders (Abdul)
 - Arrhenius (Dan)
- Current and Future Planning (Neel) ~ 3 minutes
 - Phase 3 organization

INTRODUCTION

- Key Tasks:
 - To determine the reactant order
 - Activation Energy and Arrhenius pre-exponential factor

$$Rate = k[Acetone]^{\alpha}[HCl]^{\beta}[I_2]^{\gamma}$$

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

DATA ANALYSIS

RUNS CONDITIONS

- 14 runs
- 1 standard run
- 3 runs with varying concentration for each reactant
- 4 runs with varying temperature

| Run # | Temperature (°C) | [Acetone] ₀ (M) | [HCl] ₀ (M) | [I ₂] ₀ (M) |
|----------|------------------|----------------------------|------------------------|------------------------------------|
| 1 | 35 | 2 | 0.02 | 0.0020 |
| 2 | 35 | 1 | 0.02 | 0.0020 |
| 3 | 35 | 3 | 0.02 | 0.0020 |
| 4 | 35 | 4 | 0.02 | 0.0020 |
| 5 | 35 | 2 | 0.01 | 0.0020 |
| 6 | 35 | 2 | 0.03 | 0.0020 |
| 7 | 35 | 2 | 0.04 | 0.0020 |
| 8 | 35 | 2 | 0.02 | 0.0010 |
| 9 | 35 | 2 | 0.02 | 0.0030 |
| 10 | 35 | 2 | 0.02 | 0.0040 |
| 11 | 30 | 2 | 0.02 | 0.0020 |
| 12 | 33 | 2 | 0.02 | 0.0020 |
| 13 | 40 | 2 | 0.02 | 0.0020 |
| 14 | 38 | 2 | 0.02 | 0.0020 |

ERROR PROPAGATION

- Errors in mass, absorbance, and temperature were propagated
 - Sources: Spectrophotometer, Thermocouple, and Balance
 - Reaction Orders – Method of Initial Rates
 - k – rate expression
- Errors in regression: slope and intercept
 - Rate – Least Squares
 - E_a & A – sum of squares

$$k = \frac{r_0}{[Acetone]^\alpha [HCl]^\beta [I_2]^\gamma}$$

Addition or Subtraction

$$x = a + b - c$$

$$\sigma_x = \sqrt{\sigma_a^2 + \sigma_b^2 + \sigma_c^2}$$

Multiplication or Division

$$x = \frac{axb}{c}$$

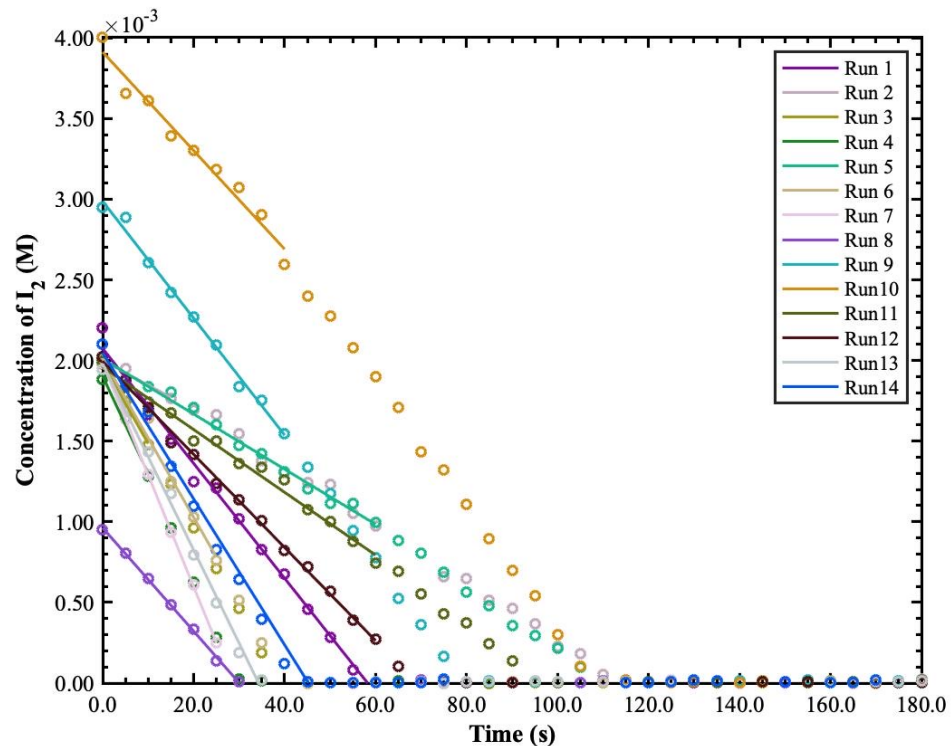
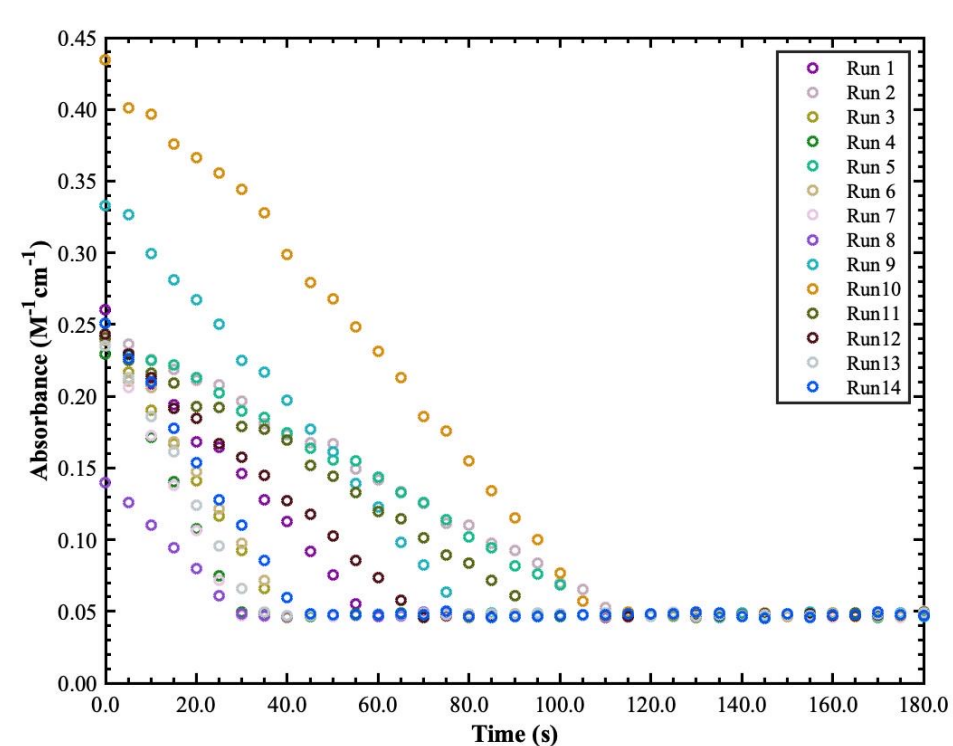
$$\frac{\sigma_x}{x} = \sqrt{\left(\frac{\sigma_a}{a}\right)^2 + \left(\frac{\sigma_b}{b}\right)^2 + \left(\frac{\sigma_c}{c}\right)^2}$$

Exponential

$$x = a^y$$

$$\frac{\sigma_x}{x} = y\left(\frac{\sigma_a}{a}\right) \quad (12)$$

INITIAL RATE METHOD



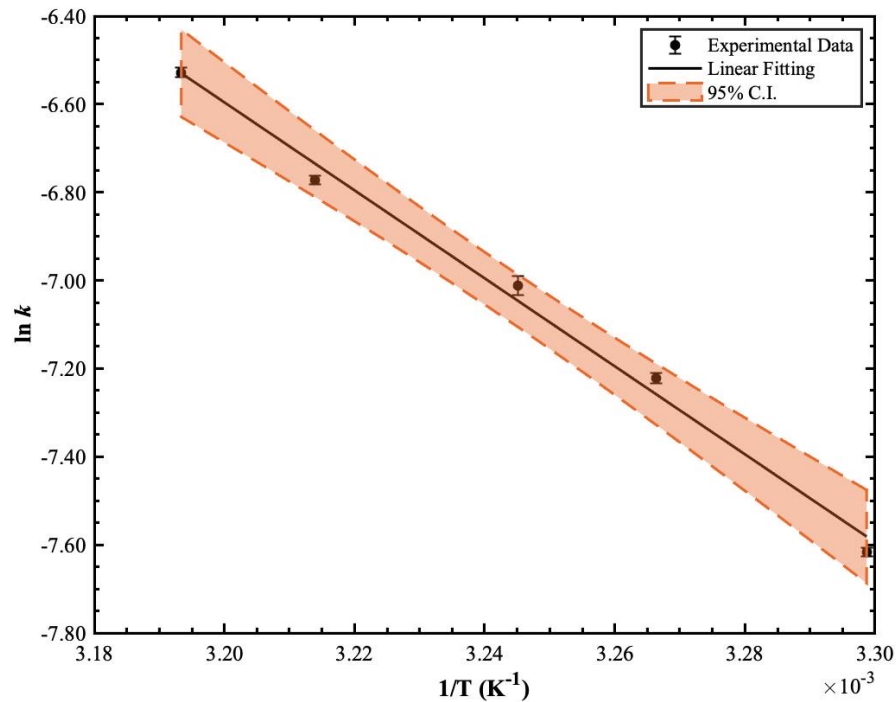
REACTION ORDERS ^a

$$r_0 = k[Acetone]^\alpha [HCl]^\beta [I_2]^\gamma$$

$$\ln r_0 = \ln k + \alpha \ln[Acetone] + \beta \ln[HCl] + \gamma \ln[I_2]$$

| Parameter | Value (95 % C.I.) | Standard Error | P-value |
|-----------|----------------------|----------------|---------|
| α | 0.9876 ± 0.5771 | 0.0210 | 0.0034 |
| β | 1.0014 ± 0.5771 | 0.0191 | 0.0031 |
| γ | -0.0003 ± 0.5771 | -0.0001 | 0.9990 |

ARRHENIUS PLOT



$$\ln k = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A$$

| Parameter | Values | 95% Confidence Interval | P-value |
|------------------------------------|------------------------|--|---------|
| A ($\text{M}^{-1}\text{s}^{-1}$) | 1.026×10^{11} | $5.951 \times 10^8 - 1.769 \times 10^{13}$ | 0.0006 |
| Ea (kJ/mol) | 83.0101 | 69.8104 - 96.2098 | 0.0003 |

PHASE III PLANNING

PLAN FOR PHASE 3

- Conduct Simulation and sensitivity analysis
 - Establish species balances to solve for the system of ODEs
 - Add iodine regeneration to Iodine balance
- Model a batch reactor and CSTR
- Analyze data and improve design
- Finalize Report

PLAN FOR PHASE 3 (cont'd)

- Part 1:
 - Use ode45 in matlab and specify the initial conditions to solve the system of differential equations.
- Part 2:
 - $\frac{d[Acetone]}{dt} = -k_1[Acetone]^{0.987} [HCl]^{1.0014} [I_2]^{-0.0003}$
 - $\frac{d[I_2]}{dt} = -k_1[Acetone]^{0.987} [HCl]^{1.0014} [I_2]^{-0.0003} + k_2[I^-]$
 - $\frac{d[HCl]}{dt} = -k_1[Acetone]^{0.987} [HCl]^{1.0014} [I_2]^{-0.0003} - 2k_2[I^-]$
 - $\frac{d[HI]}{dt} = -k_1[Acetone]^{0.987} [HCl]^{1.0014} [I_2]^{-0.0003} - 2k_2[I^-]$

TIME MANAGEMENT PLAN

Week 5, Monday, 5/03/21:

- Create MATLAB and/or ASPEN Models – Neel and Abdul

Week 6, Monday, 5/10/21:

- Prepare Final Report and Presentation – Everyone

Week 7, Monday, 5/17/21:

- Revise Final Report – Everyone



THANK YOU!

SUPPLEMENTARY A: Multiple Linear Regression

| Run # | Initial Rate, r^0 (M/s) | u^0 (M/s) | [Acetone] 0 (M) | [HCl] 0 (M) | [I $_2$] 0 (M) | ln r^0 | ln [Acetone] 0 | ln [HCl] 0 | ln [I $_2$] 0 |
|-------|---------------------------|-------------|--------------------|----------------|--------------------|----------|-------------------|---------------|-------------------|
| 1 | 3.5604E-05 | 9.1040E-07 | 2.000 | 0.020 | 0.0020 | -10.2431 | 0.6931 | -3.9120 | -6.2146 |
| 2 | 1.5291E-05 | 2.0312E-06 | 1.000 | 0.020 | 0.0020 | -11.0882 | 0.0000 | -3.9120 | -6.2146 |
| 3 | 4.9796E-05 | 2.4805E-06 | 3.000 | 0.020 | 0.0020 | -9.9076 | 1.0986 | -3.9120 | -6.2146 |
| 4 | 6.0234E-05 | 6.8145E-06 | 4.000 | 0.020 | 0.0020 | -9.7173 | 1.3863 | -3.9120 | -6.2146 |
| 5 | 1.7092E-05 | 5.0035E-07 | 2.000 | 0.010 | 0.0020 | -10.9769 | 0.6931 | -4.6052 | -6.2146 |
| 6 | 4.9220E-05 | 3.5715E-06 | 2.000 | 0.030 | 0.0020 | -9.9192 | 0.6931 | -3.5066 | -6.2146 |
| 7 | 6.9323E-05 | 3.4030E-07 | 2.000 | 0.040 | 0.0020 | -9.5767 | 0.6931 | -3.2189 | -6.2146 |
| 8 | 3.2025E-05 | 5.4560E-07 | 2.000 | 0.020 | 0.0010 | -10.3490 | 0.6931 | -3.9120 | -6.9078 |
| 9 | 3.6251E-05 | 1.1631E-06 | 2.000 | 0.020 | 0.0030 | -10.2250 | 0.6931 | -3.9120 | -5.8091 |
| 10 | 3.0549E-05 | 1.9934E-06 | 2.000 | 0.020 | 0.0040 | -10.3962 | 0.6931 | -3.9120 | -5.5215 |
| 11 | 1.9456E-05 | 6.4025E-07 | 2.000 | 0.020 | 0.0020 | -10.8474 | 0.6931 | -3.9120 | -6.2146 |
| 12 | 2.8866E-05 | 4.5988E-07 | 2.000 | 0.020 | 0.0020 | -10.4529 | 0.6931 | -3.9120 | -6.2146 |
| 13 | 5.7767E-05 | 1.6237E-06 | 2.000 | 0.020 | 0.0020 | -9.7591 | 0.6931 | -3.9120 | -6.2146 |
| 14 | 4.5263E-05 | 1.8942E-06 | 2.000 | 0.020 | 0.0020 | -10.0030 | 0.6931 | -3.9120 | -6.2146 |

| Regression Statistics | |
|-------------------------|---------|
| Multiple R | 0.86301 |
| R ² | 0.74478 |
| Adjusted R ² | 0.66821 |
| Standard Error | 0.27330 |
| Observations | 14 |

| ANOVA | | | | | |
|------------|----|---------|---------|---------|----------------|
| Parameter | df | SS | MS | F | Significance F |
| Regression | 3 | 2.17959 | 0.72653 | 9.72718 | 0.00260 |
| Residual | 10 | 0.74691 | 0.07469 | | |
| Total | 13 | 2.92650 | | | |

| Parameter | Coefficients | Standard Error | t Stat | P-value | Lower 95% | Upper 95% |
|-------------------|--------------|----------------|---------|---------|-----------|-----------|
| Intercept | -7.0739 | 1.9086 | -3.7063 | 0.0041 | -11.3266 | -2.8213 |
| ln [Acetone] $_0$ | 0.9876 | 0.2590 | 3.8129 | 0.0034 | 0.4105 | 1.5647 |
| ln [HCl] $_0$ | 1.0014 | 0.2590 | 3.8662 | 0.0031 | 0.4243 | 1.5785 |
| ln [I $_2$] $_0$ | -0.0003 | 0.2590 | -0.0012 | 0.9990 | -0.5774 | 0.5768 |