

# **Deducing the Mechanism of an Unknown System of Reactions**

James Lipe

Emma Pierce

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Professor West

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Northeastern University

# 1. Introduction

The purpose of this investigation is to deduce the mechanism of a system of unknown elementary reactions. The controlled variables are the concentrations of reactant “A” and catalyst “C” as well as the operating temperature and the interval at which data is collected over time. The following report details the experimental methods and procedures that were used to determine the reaction mechanism, the constants involved, and safe operating parameters as well as addressing any unknowns and suggestions for further analysis.

## 2. Determining the Presence of a Catalyst and Intermediate

In each of the experiments performed with the catalyst, the concentration of reactant A is depleted. In the complete absence of catalyst, no reaction occurs. This suggests that the first elementary reaction is  $A + C \rightarrow \text{some product}$ . Since the concentration of A is depleted to zero mol/L as time increases to infinity, it is a reasonable assumption that at least one of the reactions consuming A is not reversible.

$$N_{Ai} = N_A + N_D + N_U \quad \text{Eqn. (1)}$$

$$N_I = N_{Ai} - N_A - N_D - N_U \quad \text{Eqn. (2)}$$

The presence of an intermediate was determined using a mole balance at each data point (Eqn. (1)). Since the amount of reactant A is not equal to the combined amount of desired product, D, and undesired product, U, there must be an intermediate species, I (Eqn. (2)). The concentration of I is low relative to that of A, D, and U and is depleted almost immediately (Fig. (1)). This suggests that it is being consumed approximately as fast as it is being produced. Since the concentration is depleted to zero mol/L by the end of the reaction, it can be concluded that at least one of the reactions consuming I is irreversible.

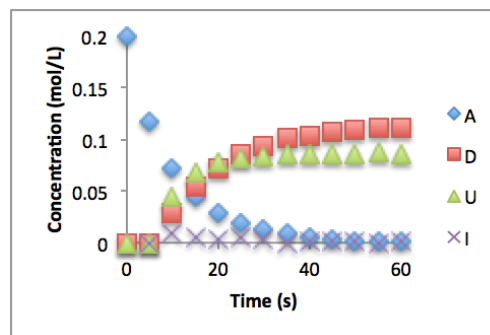


Fig. (1): The concentration of each species

## 3. Deducing the Elementary Reactions

Trials run at different starting concentrations and temperatures provide enough data points to propose a system of elementary reactions and determine the order of each. The proposed mechanism is:



The stoichiometry of the reactions is determined by the assumption that species A, C, D, and U have approximately the same molar mass. Since the intermediate is the combination of A and C, conservation of mass dictates that  $\text{g/mol}_I = 2 \text{ g/mol}_A$ . An overall species balance yields the shown stoichiometric coefficients.

### 3.1 Confirming Reaction (1)

To support Rxn. (1), [A] and C can be plotted against  $(r_A + 0.5r_U)$  to give a linear slope. This slope represents the rate constant for the forward reaction,  $k_1$ . The reaction was run at 25°C with nine different starting concentrations of A, and the  $k_1$  values averaged to find improve accuracy. The rate constant at 15°C is  $k_1 = 0.227 \pm 0.003 \text{ dm}^3/(\text{mol.s})$ , as shown in Fig. (2). The rate constant of the reverse reaction,  $k_{-1}$ , is essentially negligible due to the immediate consumption of I.

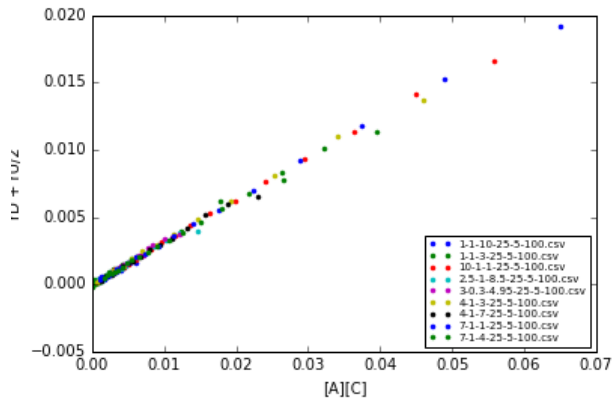


Fig. (2): The rate constant at 15°C

### 3.2 Confirming Reaction (2)

Initial investigations of Rxn. (2) suggested that it was a zero order reaction. Further research concluded that it was a pseudo zero order reaction that follows Michaelis-Menten kinetics. The plot of  $r_D$  vs. [I] supports this theory and its slope gives the rate constant  $k_2$ , shown in Fig. (3). The same multiple trial averaging method was used to yield an accurate value of  $k_2 = 0.34 \pm 0.04 \text{ s}^{-1}$  at 15°C.

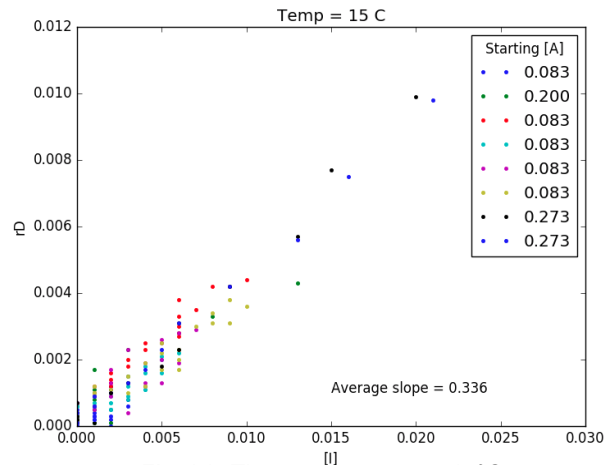


Fig. (3): The rate constant at 15°C

### 3.3 Confirming Reaction (3)

A method similar to that of Section 3.1 was taken to confirm Rxn. (3). The reaction rate  $r_U$  was plotted against  $([A]*[I])$  to give a linear trend. The trial was repeated at 15°C with two different starting concentrations, giving an average slope of  $k_3 = 2.51 \pm 0.07 \text{ s}^{-1}$  as shown in Fig. (4).

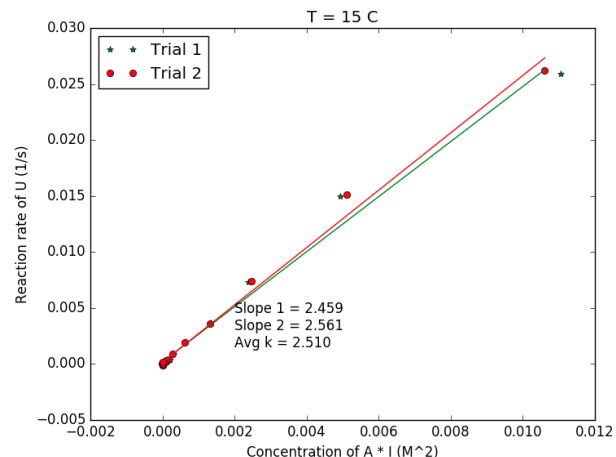


Fig. (4): The rate constant at 15°C

## 4. Changing Temperatures and Finding the Activation Energies

The rate constants were each calculated at three temperatures. This data can be used to determine each constant's dependence on temperature as well as to calculate the activation energy,  $E_A$ .

### 4.1 Rate Dependence on Temperature

The rate constants can be expressed as functions of temperature as the following:

$$k_1(T) = 0.007 * T + 0.14 \text{ dm}^3/(\text{mol} \cdot \text{s}) \quad \text{Rxn. (1)}$$

$$k_2(T) = 0.008 * T + 0.22 \text{ s}^{-1} \quad \text{Rxn. (2)}$$

$$k_3(T) = 0.087 * T + 1.2 \text{ s}^{-1} \quad \text{Rxn. (3)}$$

The equilibrium constant cannot be calculated because the reaction runs until it consumes all of reactant A and intermediate I. The reaction as a whole does not reach equilibrium, and the equilibrium constant of Rxn. (1) cannot be calculated because the reverse rate cannot be calculated.

Supplemental data and figures showing the rate constants as slopes of a linear plot can be found in Appendix A.

### 4.2 Activation Energies

The rate constants and temperatures in section 4.1 can be used to calculate the activation energy of each elementary reaction using Eqn. (3).

$$\ln \left( \frac{k_2}{k_1} \right) = \frac{-E_A}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{Eqn. (3)}$$

The individual calculated values can be found in Appendix B. The average activation energies are  $E_{A1} = 19 \pm 2 \text{ KJ/mol}$ ,  $E_{A2} = 15 \pm 1 \text{ KJ/mol}$ , and  $E_{A3} = 37 \pm 1 \text{ KJ/mol}$ . The small standard deviations indicate that the proposed mechanism is accurate.

## 5. Model Parameters and Safety Concerns

The optimal running temperatures of the reaction for the purposes of deducing the mechanism were  $-5^\circ\text{C}$  to  $25^\circ\text{C}$ . Lower temperatures cause the reaction to slow down, requiring a longer period of time to collect enough useful data points, therefore making it more expensive due to manpower.

It is best for the purposes of this investigation to use a ratio of  $dL_A$  to  $dL_C$  that does not exceed 10. The initial elementary reaction is too dependent on the catalyst that having a larger ratio slows the reaction down considerably.

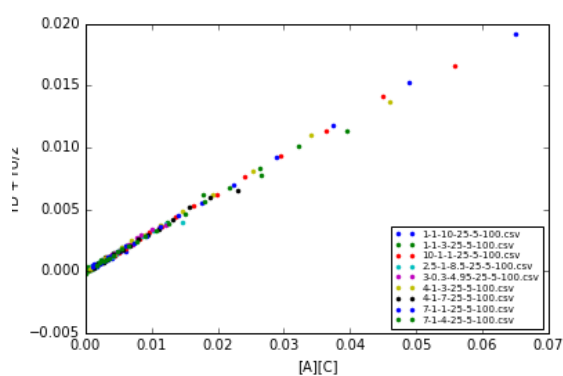
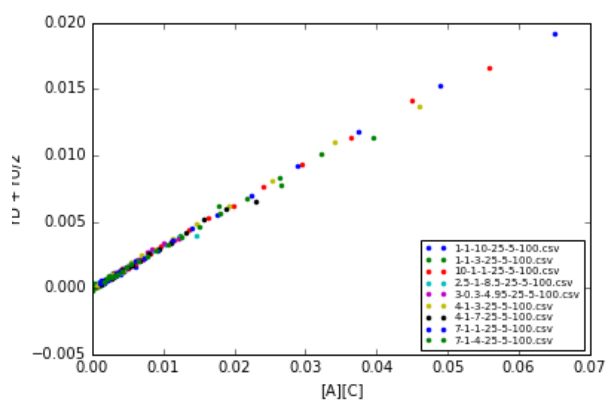
It was determined during experimentation that the solvent combusts at 200°C. For safety reasons it is not recommended to run the reaction above 150°C. The solvent also freezes at temperatures below -21°C, so caution should be taken when operating at extremely low temperatures.

## **6. Conclusions**

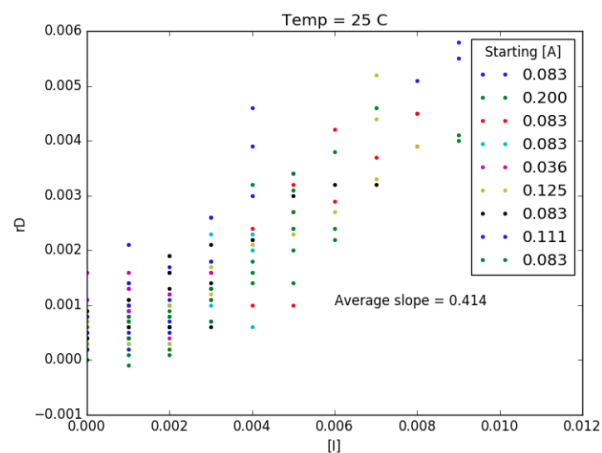
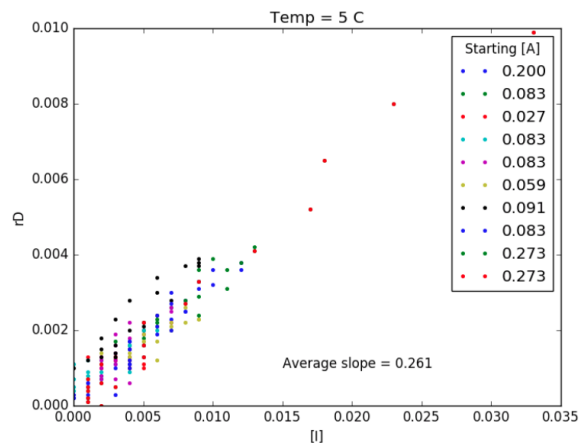
When the reaction is run with a small ratio of reactant A to catalyst C, the desired product dominates the reaction. To yield the most consistent results, the temperature should be kept between -5°C and 25°C. The activation energies and their small errors support the proposed mechanism. The majority of the calculations and plots were performed in a Python program, which can be found in Appendix C and is included with this report.

## Appendix A: Supplemental Rate Constant Data

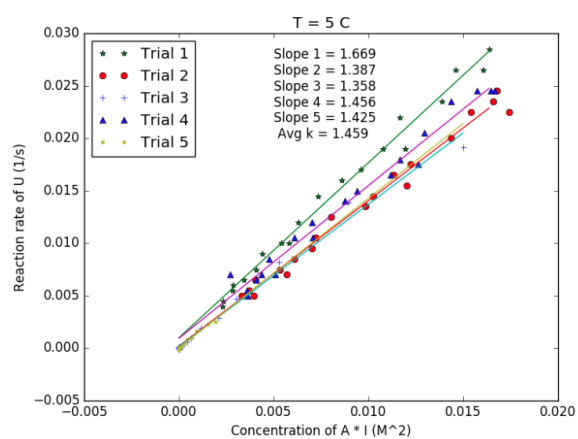
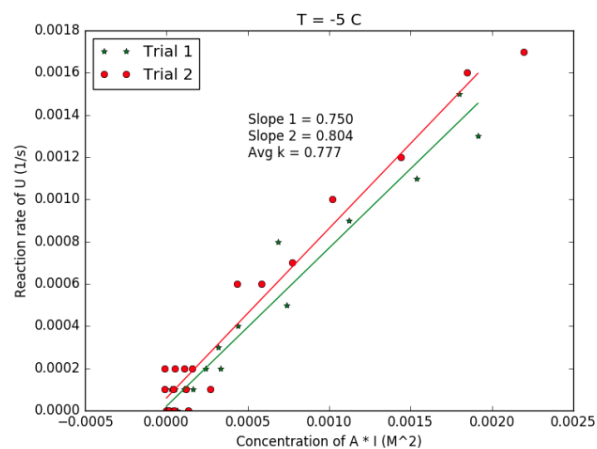
Rate constants for Rxn. (1) at 5°C and 25°C:



Rate constants for Rxn. (2) at 5°C and 25°C

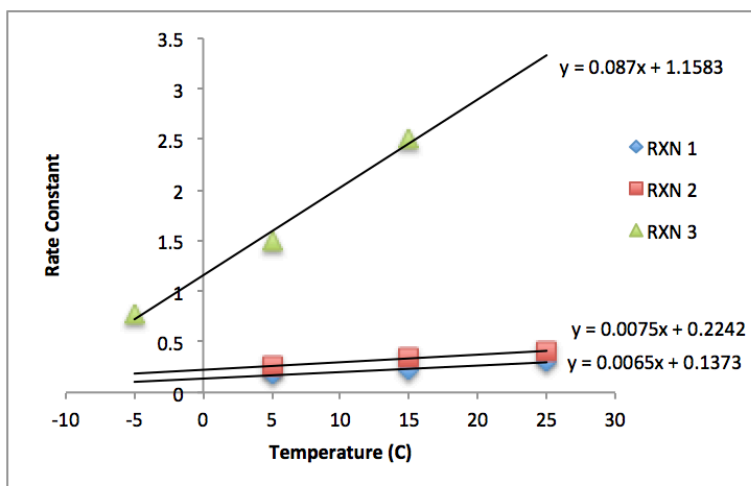


Rate Constants for Rxn. (3) at -5°C and 5°C



Rate constant data table and dependence on temperature plot:

Temp (°C)	$k_1$ dm <sup>3</sup> /(mol.s)	StDev	$k_2$ s <sup>-1</sup>	StDev	$k_3$ s <sup>-1</sup>	Stdev
-5					0.77	0.02
5	0.173	0.004	0.26	0.01	1.5	0.2
15	0.227	0.003	0.34	0.04	2.51	0.07
25	0.302	0.004	0.41	0.03		



## Appendix B: Activation Energy Data Table

Reaction	$T_1$ (°C)	$T_2$ (°C)	$E_A$ (KJ/mol)	Average (KJ/mol)	StDev (KJ/mol)
1	5	15	18.30	19.4	1.10
	5	25	19.30		
	15	25	20.50		
2	5	15	16.84	15.9	0.96
	5	25	15.91		
	15	25	14.92		
3	-5	5	39.09	37.6	1.47
	-5	15	37.66		
	5	15	36.15		