

**KINETICS OF AUTOCAUSTICIZATION USING BORATES IN A  
BLACK LIQUOR GASIFICATION PROCESS**

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By

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KINETICS OF AUTOCAUSTICIZATION USING BORATES IN A BLACK  
LIQUOR GASIFICATION PROCESS

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## LIST OF SYMBOLS

### Roman Nomenclature

a	interfacial area per unit volume
C	concentration
$E_i$	energy
H	Henry's constant
J	number of data points
$k_i$	mass transfer coefficient
$k_i$	reaction rate constant
K	pre-exponential factor for the Arrhenius Rate Equation
Mw	molecular weight
$P_i$	partial pressure
R	gas constant
$R_i$	rate
S	difference between model and data values
T	temperature
t	time
$V_i$	volume
X	conversion

## **Greek Nomenclature**

$\Delta H$	heat of reaction
$\Sigma$	sum
$\sigma$	standard deviation

## **Symbols**

[ ]	concentration, L/mol
-----	----------------------

## **Subscripts**

1	forward reaction
-1	reverse reaction
o	initial condition
a	activation
CO <sub>2</sub>	carbon dioxide
L	liquid

## SUMMARY

The path of research in the pulp and paper industry is heading towards the elimination of the lime cycle, which requires large amounts of energy, and changing the conventional recovery boiler system to a gasification process that will reduce the possibility of smelt water explosions while meeting future environmental regulations. Research has been carried out on both gasification processes and on causticizing processes that can replace or complement the lime cycle, however very little research has gone into the actual kinetics of causticization using black liquor in gasification processes. This research project fills in some of the missing knowledge in the area of kinetics of auto-causticization reactions, which entails the use of borates as the auto-causticizing agent. A temperature dependent kinetic model coupled with a mass transfer coefficient has been developed and compared to experimental data.

## CHAPTER 1

Alternatives to traditional black liquor recovery are being considered due to the disadvantages of the conventional recovery processes. Current shortcomings of the traditional process include high operating costs and low efficiency: The capital for a kraft recovery boiler is around a \$100 million [1], making it the most expensive piece of equipment in the pulp mill and internally, a pulp mill only produces about 50% of its own power requirements. Furthermore, with the possible addition of black liquor gasification to the recovery process, alternative causticization methods will have to be developed to meet increased causticization loads. One method of meeting the increased demand is by auto-causticization using borates, either as a full auto-causticization unit or as a partial (add-on to the conventional recovery process) auto-causticization unit. This study entails analysis of the kinetics to determine completion times, rates, influencing factors such as temperature and mass transfer, and ultimately, developing an adequate model that describes the chemistry, kinetics and mass transfer, of the system. Overall, kinetics of auto-causticization will benefit the paper industry by illustrating the possibility of using a different recovery process that can either aid or replace the current processes, while being less costly, more efficient, and in-turn, more environmentally friendly.

### **1.1. Conventional Kraft Pulping and Black Liquor Recovery Process**

The purpose of kraft pulping is to separate the cellulose fibers from lignin in the wood in the most economically feasible manner. Lignin and other organic substances are

dissolved from the wood pulp during the kraft pulping process. Wood chips are mixed with white liquor, containing the pulping chemicals, mainly hydroxide ions and hydrogen sulfide ions. After the digestion, most of the cellulose is still in the solid phase (i.e. the pulp), whereas the lignin and the spent pulping chemicals are in the liquid phase, which is called black liquor. The pulp is separated from the black liquor and is then washed. The black liquor is then burnt as its organic material content has a high heating value, nominally around 6000 BTU/lb black liquor solids [1], which can be used to produce steam or electricity.

Before the black liquor can be burned or gasified, the water content in the black liquor has to be considerably decreased. The dry solids content of the black liquor is increased from 15% to over 70% using multiple-effect evaporation. The concentrated liquor, now identified as heavy black liquor, in the conventional recovery process, is sprayed into to the recovery boiler and burned. The large amount of heat released in the recovery boiler, is used to produce superheated steam; simultaneously the sodium and sulfur in the black liquor are converted to sodium carbonate and sodium sulfide, forming an inorganic smelt. The smelt is removed from the bottom of the recovery boiler and is dissolved in weak wash to make green liquor.

After the dregs have been removed from the green liquor through clarification or filtering, it is sent to the slaker. The clarified green liquor is then reacted with lime, CaO.



The product of the slaking reaction, calcium hydroxide, is washed and sent to the causticizers where it reacts with sodium carbonate, releasing sodium hydroxide and lime mud – CaCO<sub>3</sub>.



The white liquor then goes through a clarification process to separate the liquor from the lime mud. The clarified white liquor is recycled and sent to the digesters. The lime mud is brought to the lime kiln where it is calcined to reform lime. The lime kiln requires a lot of heat, supplied by purchasing natural gas or fuel oils at the order of 5-8 Million BTU/ton CaO [1].



Besides the inefficiency of the lime kiln, the conventional kraft recovery cycle has many drawbacks: The equilibrium of the causticizing reaction produces a dead-load of sodium carbonate that increases the energy requirement of the entire pulp process; there is an explosion risk when the sodium sulfide and sodium carbonate smelt is dissolved in the dissolving tank; and the heat recovered from the recovery boilers is recuperated only as steam.

## **1.2. Alternative Recovery Processes**

The current drawbacks of the conventional recovery process highlighted above are the rationale for research on possible alternative recovery processes. In order to harness more of the energy that is released from the black liquor's organic material, gasification processes are being considered. The large amount of energy that is required by the lime

cycle has brought attention to the possibility of actually annulling it by the use of new causticizing processes.

### **1.2.1. Gasification Processes**

The main notion of gasification is the partial-burning of the organic and inorganic materials in the black liquor. In order to be beneficial to the industry, the inorganic chemicals should be recovered and recycled as green liquor and the organic materials should be gasified to form a combustible product gas, which can be used to create energy, both as heat and electricity. The product gas is produced by burning the black liquor with lower concentrations of air, so that only partial combustion takes place [2]. Successful gasification of black liquor produces a near 100% conversion of carbon into carbon monoxide, carbon dioxide and methane; other released gases are hydrogen gas, water and hydrogen sulfide. There are two basic types of gasification processes that are used in the recovery of black liquor:

1. Low temperature - fluidized bed  
< 715 °C  
Inorganic salts are removed as dry solids
2. High temperature - entrained flow reactor  
> 900 °C  
Inorganic salts form a smelt

There are many types of gasification processes that are being or have been tested over the last decade, the Chemrec and the MTCI processes being the most advanced [3].

However, it is important to stress that the current gasification processes have a lower overall energy efficiency than the conventional system if the product gases are burned in a power boiler. Because of this, some research has focused on electrical power generated from gas turbines – which can yield a higher net electrical power generation than what would be possible from the conventional cycle [3].

### **1.3. Alternative Causticization Processes**

There are two basic types of alternative causticization processes that are being considered: direct causticization and autocausticization processes. In both cases an oxide is used as the causticizing agent. If the oxide is soluble in water it is called autocausticization and direct causticization if insoluble.

#### **1.3.1. Direct Causticization**

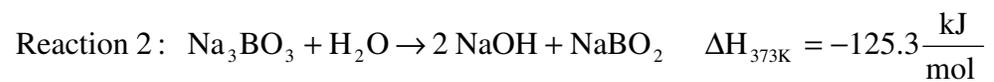
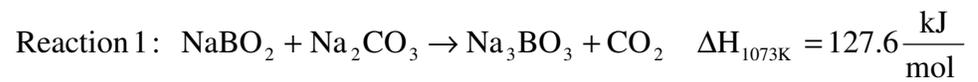
In direct causticization the oxide is insoluble in alkaline solutions and precipitates during the dissolution phase. The causticizing agent is a metal oxide agent, such as titanium oxide, manganese oxide, and iron oxide. The hydrated metal oxide complex can easily be recovered from the white liquor and be recycled. Overall advantages to direct causticization include the elimination of the lime cycle, reduction in dead-load of sodium carbonate, and the high concentration of sodium hydroxide in the recovered white liquor. However, the price of metal oxide causticizing agents can be quite high and the possible dead-load of metal oxide is not known. Also a method of separating the dregs from the

recycled metal oxide has to be developed in order for direct causticization to be a viable option.

### **1.3.2. Autocausticization**

The kraft pulping process has taken over the pulping industry as its superior pulp quality has made it more desirable than sulfite pulping. Despite the obvious benefits of kraft pulping, there have been numerous studies aimed at the inferior properties. Some of these inferior properties include the low yield, low pulp brightness, and the complicated liquor cycle. The initial target was the sodium hydroxide that is responsible for the delignification of the wood: another inorganic, sodium compound would have to be found that reacted with lignin in a similar manner. The second target would be to circumvent the high energy costs of the causticizing cycle, by recycling the spent green liquor as the original white liquor. In order to recycle green liquor as white liquor, the delignifying agent has to be able to go through a sequence of reactions, during the combustion of black liquor, resulting in the original inorganic compound without the addition of chemicals; this was termed autocausticization [4].

There are numerous chemicals that can be used as autocausticizing agents, such as borate, silica, and disodium phosphate [5]. However, borates are the most feasible autocausticizing chemicals as they are water-soluble, the decarbonization of  $\text{Na}_2\text{CO}_3$  and the hydrolysis of sodium borates occur rapidly in aqueous solution, and they do not react with sulfide in the smelt. The two autocausticizing reactions of sodium borates are listed below [6]:



From the reactions above, it is clear that the process is very appealing as sodium hydroxide is directly produced in the white liquor, eliminating the need for the conventional causticizing cycle – consisting of the slaker, causticizers, and lime kiln.

## CHAPTER 2

### 2.1. Delignification

Sodium borate is a suitable delignifier as its pH range lies between 14 and 11.5, which is greater than what is required for delignification to take place. Through the experimentation with various wood species, Janson [7] found that sodium borate delignified wood at around the same rate as NaOH and at low alkali concentrations faster than sodium hydroxide. The greatest benefit of sodium borate was found when the product white liquor was recycled and found to delignify almost as well as the original liquor. Janson [8] also revealed that the sodium borate pulp's brightness was similar to that of the sodium hydroxide pulp. It was also found that the viscosity of the product was equal to or greater than that of kraft pulp. The low heating values of the spent borate liquors and the lower yield compared to kraft pulping were the two major detriments of sodium borate. However, probably the most interesting result was illustrated by the reduced need of sodium borate compared to sodium hydroxide [9]. Other benefits such as better quality pulp and less shrinkage during bleaching were found later by Tran et al [10].

### 2.2. Full versus Partial Causticization

There are two basic concepts of the autocausticization process that have been studied over the last thirty years: the full autocausticization and the partial autocausticization processes.

Full auto-causticizing completely eliminates the causticizing units of the chemical recovery cycle and depends only on the ability of the borate to completely convert the carbonate to hydroxide. The problem with full auto-causticization is that a high amount of borate has to be used, however, it has been found that decreasing the amount of borate versus sodium in the system ( $\text{Na/B} > 3$ ), can be beneficial for a partial auto-causticization process [11]. A partial process still depends on the causticizing of calcium carbonate, but an increase in production rate and the addition of smaller amounts of borates can actually reduce the strain on the lime cycle [11]. The full process will easily take advantage of the auto-causticizing abilities of sodium borate, but the partial auto-causticization process can be a very beneficial addendum to existing process lines as very little additional equipment has to be used.

### **2.3. Previous Kinetic Studies**

Research carried out by Tran, et al, [10], studied the reaction of sodium borate and sodium carbonate in a radio-frequency induction furnace. The conversion was measured by monitoring the amount of carbon dioxide released while continuously purging the system with nitrogen gas. Purging the sample with nitrogen strips the excess carbon dioxide formed during the reaction, which basically causes the reaction to become a second order irreversible reaction. Through further studying, it was found that the conversion was severely retarded if the carbon dioxide was not continuously stripped. This suggests that the system is in fact reversible. Nonetheless, it was [10] suggested the rate of reaction to be:

$$\frac{d[\text{CO}_2]}{d t} = K \exp\left(-\frac{E_a}{RT}\right) [\text{NaBO}_2][\text{Na}_2\text{CO}_3]$$

where

$$K = 2580 \pm 400 \frac{\text{L}}{\text{mol} \cdot \text{s}}$$

$$E_a = 35 \pm 2.5 \frac{\text{Kcal}}{\text{mol}}$$

If the reaction is truly reversible, then the following rate should be observed:

$$\frac{d[\text{CO}_2]}{d t} = k_1 [\text{NaBO}_2][\text{Na}_2\text{CO}_3] - k_{-1} [\text{Na}_3\text{BO}_3][\text{CO}_2]$$

where

$k_1$  = forward reaction rate constant

$k_{-1}$  = reverse reaction rate constant

## CHAPTER 3

### 3.1. Objectives

Autocausticization using sodium borates as the autocausticizing agent in a black liquor gasification process can be very beneficial in the future to reduce or even eliminate the need for the energy-consuming lime kiln. It is important to focus on the gasification process as it will probably replace the conventional kraft recovery boilers in the future [12]. Before autocausticization and gasification can be used collectively, kinetic research has to be done on the sodium borate and sodium carbonate reaction. The purpose of this study is to evaluate the reaction kinetics at temperatures below and above the melting point of sodium carbonate and to develop a kinetic model to estimate the activation energy of the forward reaction.

### 3.2. Experimental Conditions

In order to understand the kinetics of autocausticization in black liquor, it is important to understand the reaction between sodium borate,  $\text{NaBO}_2$ , and sodium carbonate,  $\text{Na}_2\text{CO}_3$ . When sodium borate and sodium carbonate react together trisodium borate and carbon dioxide are produced, (see Reaction 1) [9]. By measuring the weight loss or the amount of carbon dioxide released during the course of the reaction, the conversion can be determined.

The temperature range for which gasification processes are currently being developed is from 600°C to 1000°C, and since the melting point of sodium borate is around 851°C,

the 800°C to 925°C temperature range was chosen. At each experimental condition, enough runs will be carried out to show reproducibility.

## CHAPTER 4

### 4.1. Kinetic Model

The kinetic model that will be used will depend on the phase of the system; this could range from a liquid phase reaction to fluid-solid or even solid-solid reactions. From previous research [11, 13], it has been illustrated that carbon dioxide severely dampens the overall conversion rate of the reaction. This shows reversibility: when a product of the reaction is introduced to the system, the equilibrium of the reaction is shifted towards the reactants, according to the Le Chatelier's Principle. So, for the autooxidation reaction rate, for a fluid – solid system, the following reversible, second order kinetic expression is developed:

$$R_{\text{Reaction}} = k_1 C_O^2 \cdot (1 - X)^2 - k_{-1} C_O X \cdot C_{\text{CO}_2}$$

where

$k_1$  = forward reaction rate constant

$k_{-1}$  = reverse reaction rate constant

$C_O$  = initial concentration of reactants

$X$  = reaction conversion

$C_{\text{CO}_2}$  = concentration of  $\text{CO}_2$  in the liquid phase

The difficulty of this reaction is the fact that the concentration of carbon dioxide in the liquid phase at any given time is not known. However, it is known that the solubility of a gas in a liquid decreases with temperature and is thus expelled from the liquid phase. This introduces a mass transfer term to the system:

$$R_{\text{Mass Transfer}} = k_L a V_L \cdot (P_{\text{CO}_2} - P_{\text{CO}_2}^{\infty}) = k_L a V_L H \cdot C_{\text{CO}_2}$$

where

$k_L$  = liquid mass transfer coefficient

$a$  = surface area per unit liquid volume

$P_{\text{CO}_2}$  = partial pressure of  $\text{CO}_2$

$P_{\text{CO}_2}^{\infty}$  = ambient partial pressure = 0

$H$  = Henry's constant

$V_L$  = liquid volume

From the mass transfer equation above, the total amount of carbon dioxide produced during the course of the reaction can be expressed as:

$$V_L C_O \cdot X = \int_0^t R_{\text{Mass Transfer}}(t) \cdot dt + V_L \cdot C_{\text{CO}_2}$$

The term  $V_L \cdot C_{\text{CO}_2}$  is assumed to be negligible compared to the amount of carbon dioxide released to the gas phase, so it is eliminated from the equation.

$$V_L C_O \cdot X = \int_0^t R_{\text{Mass Transfer}}(t) \cdot dt$$

Differentiating both sides of this equation with respect to time yields an expression in terms of conversion and the concentration of carbon dioxide in the liquid phase:

$$V_L C_O \cdot \frac{dX}{dt} = k_L a V_L H \cdot C_{\text{CO}_2}$$

or

$$\frac{C_O}{k_L a H} \frac{dX}{dt} = C_{\text{CO}_2}$$

Using the previous expression for dissolved carbon dioxide and substituting it into the overall reaction rate expression, it can be rewritten to form:

$$C_o \frac{dX}{dt} = k_1 C_o^2 \cdot (1-X)^2 - k_{-1} C_o X \cdot \frac{C_o}{k_L aH} \frac{dX}{dt}$$

since

$$C_o X = CO_2$$

The previous equation can then be simplified:

$$\frac{dX}{dt} = k_1 C_o \cdot (1-X)^2 - \frac{k_{-1} X \cdot C_o}{k_L aH} \frac{dX}{dt}$$

and solving for  $\frac{dX}{dt}$

$$\frac{dX}{dt} = \frac{k_1 C_o \cdot (1-X)^2}{1 + \frac{k_{-1} X \cdot C_o}{k_L aH}}$$

This final expression can be rewritten by substituting

$$\alpha = k_1 C_o$$

and

$$\beta = \frac{k_{-1} \cdot C_o}{k_L aH}$$

and forming:

$$\frac{dX}{dt} = \frac{\alpha \cdot (1-X)^2}{1 + \beta X}$$

#### 4.2. Marching Ahead Technique

The equation for the conversion above is extremely difficult, if not impossible, to solve for X. So in order to solve for the parameters of the expression a different method

will have to be used. A numerical method called the Marching Ahead technique, also known as Euler's Method [13], can be used to solve the expression. The Marching Ahead technique splits up the course of the reaction into small time increments,  $\Delta t$ . The differential equation can then be made into an approximate linear equation by:

$$\frac{dX}{dt} = \frac{\alpha \cdot (1 - X)^2}{1 + \beta X}$$

and applying the Marching Ahead technique

$$X_t = X_{t-\Delta t} + \frac{\alpha \cdot (1 - X_{t-\Delta t})^2}{1 + \beta X_{t-\Delta t}} \Delta t$$

$$t = t + \Delta t$$

In this expression, it is important that the time increment is small enough to reduce the systematic error associated with using the Marching Ahead technique. The Marching Ahead equations can then be applied to a simple programming language, such as Basic, which will solve for the parameters of the equation. Using programming languages to match the expression to kinetic data is very beneficial, as the computer can run through thousands of iterations in a few seconds. The program, or macro, can be coupled with a least-squares analysis to insure that the best fitting parameters are found.

### **4.3. Statistical Analysis**

A least-squares analysis [13] will be performed for each run and for all temperatures, in order to disclose the accuracy of the model versus the actual data points. This is done by calculating the residual sum of squares:

$$S_{\text{residual}}^2 = \sum_{j=1}^J (\text{data} - \text{model})^2$$

where J is the number of data points

The residual sum of squares is then used to calculate the residual standard deviation of the model versus the data:

$$\sigma_{\text{residual}} = \sqrt{\frac{S_{\text{residual}}^2}{J-1}}$$

The residual sum of squares should be approximately the experimental error, if it is too low, the model has too many variables or didn't use enough data points.

#### 4.4. Evaluating the Rate Constants

The best-fitting parameters of the reaction conversion expression can be found at different temperatures and then used to evaluate the forward rate constants. The reverse rate constants cannot be differentiated from the beta term, as  $k_{-1}$ ,  $k_L$ , and H are all functions of temperature and are unknown. The forward rate constant should be in the general form of the Arrhenius equation:

$$k = K \cdot e^{-\frac{E_a}{RT}}$$

In this equation k is the rate constant, K is the pre-exponential factor,  $E_a$  is the activation energy, R is the gas constant, and T is the temperature in Kelvin. The factor  $E_a/R$  can be substituted by the term  $T^{\text{act}}$ , which is called the activation temperature:

$$k = K \cdot \exp\left(-\frac{T^{\text{act}}}{T}\right)$$

By plotting the negative of the natural log of the rate constant versus inverse temperature (in Kelvin), a straight-line plot should be achieved. Fitting a linear trendline through the data points will yield the activation temperature from the slope and the pre-exponential factor from e raised to the power of the intercept.

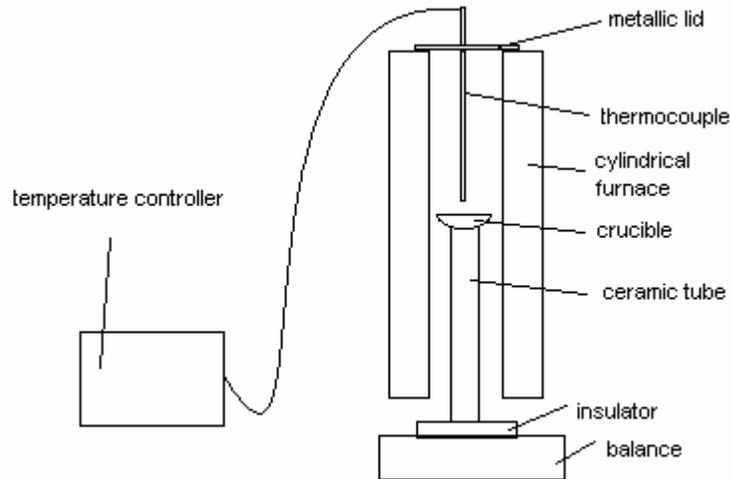
## CHAPTER 5

### 5.1. Sample Preparation

Sodium metaborate and sodium carbonate were dissolved in distilled water, according to the stoichiometric ratio of the reaction (1:1). The mixture was then heated to its boiling point in order to remove the water from the solution. As the solution thickened, it became increasingly difficult to keep the system well stirred. When the magnetic stirrer could no longer turn, the mixture was placed on a Teflon pan and left in a 110°C oven to dry overnight. When the sample was sufficiently dry, it was removed and placed in a jar for grinding. The following day, the powder was removed from the jar and placed in a sieve with a 53 micron size-fraction. The powder that passed through the sieve was the reactants that were going to be used in the reaction.

### 5.2. Apparatus

- 1 Cylindrical furnace with external controller:



- 2 Thermocouple to measure the temperature inside the furnace.
- 3 Zirconium crucibles.
- 4 Ceramic tube to hold crucible inside the furnace.
- 5 Insulator to protect the balance from the high-temperature ceramic tube.
- 6 Balance with 0.01 gram increments to measure weight loss during the course of the reaction.
- 7 Stopwatch to keep time.

### 5.3. Procedure

The furnace was first turned on and set to a specific temperature. The sample was weighed out and placed in a zirconium crucible, which was then placed on top of the ceramic tube. The ceramic tube was carefully inserted through the bottom of the furnace, as not to lose the high temperature through the top of the furnace. The ceramic rod was then placed on top of an insulator and then on the balance. The balance was tared and the

stopwatch was started. As the balance was very sensitive to pressure and wind fluctuations in the lab, a shield was placed around it. For the first initial runs, the thermocouple was pushed down far enough without influencing the balance readings. As the reaction was proceeding, the time was recorded every 0.05 grams of mass loss. The reaction was allowed to proceed until no mass loss was observed in a significant amount of time, usually 10 minutes. The reactions were done at 800, 825, 875, 900 and 925°C and repeated until reproducibility could be shown.

## CHAPTER 6

### 6. Results and Discussion

During the preparation of the sample, it was found that it was very difficult to remove all of the water through drying. This was probably caused by some of the sodium borate forming hydrates, which require higher temperatures for complete removal of water. The hydrated water was removed during the initial stage of the reaction, and it was assumed that the reaction only took place once all the water was removed.

#### 6.1. Conversion of Sodium Carbonate

The conversion of sodium carbonate to carbon dioxide was calculated from the mass loss of the reactions. Since the only source of mass loss during the reaction was the released carbon dioxide gas, the maximum mass loss percentage would be:

$$\frac{Mw_{\text{Carbon Dioxide}}}{Mw_{\text{Sodium Borate}} + Mw_{\text{Sodium Carbonate}}} = \frac{44.01 \frac{\text{g}}{\text{mole}}}{65.80 \frac{\text{g}}{\text{mol}} + 105.99 \frac{\text{g}}{\text{mol}}} = 25.62\%$$

The conversion at a specific time was then calculated using this maximum conversion by:

$$\text{Conversion} = \frac{\text{Mass}_{\text{loss}}}{\text{Mass}_{\text{initial}} \cdot (0.2562)}$$

The following figure illustrates the conversion versus time for specific temperatures:

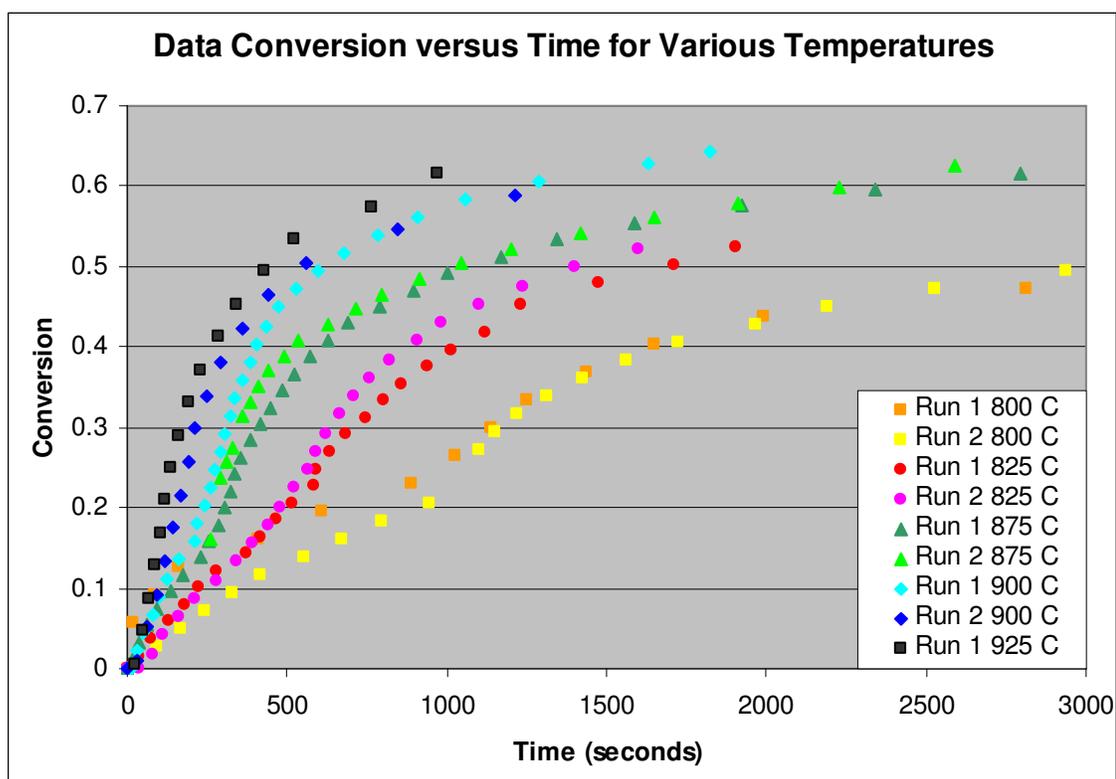


Figure 1: Conversion versus Time for Various Temperatures

It is quite obvious from the previous figure (Figure 1), that there are two parts to each reaction run. The first phenomenon that takes place is a non-isothermal heating of the reactants, and then a phase change occurs. Previous research [12] indicated that below the melting point of sodium carbonate, the reactions take place as a solid-solid reaction. However, during this study, it was always observed that the reactions took place in a liquid state, which contradicts the previous research. Previous studies might not have found this melting point depression as they did not keep the system at a constant temperature long enough for melting to occur. An other reason could be that the melting temperature for a one-to-one molar ratio of sodium carbonate and sodium borate is lower

than other ratios. In order to analyze the actual isothermal, liquid-liquid reaction that takes place, the first curve was eliminated from all kinetic modeling.

## 6.2. Kinetic Modeling

The Marching Ahead approach, discussed in the Modeling section, was used to determine the parameters of the system. A random search macro was used to find the values of alpha and beta so that the smallest residual sum of squares could be found, see appendix for the macro. The random search and Marching Ahead technique was used for every run, and the alpha and beta constants were averaged for individual runs at the same temperatures. Since equimolar mixtures of sodium borate and sodium carbonate were charged to the crucible, the initial concentration,  $C_0$  was assumed constant and equal to 50% of the molar density of liquid sodium carbonate: 9.2 Moles/Liter. This enabled calculations of both  $k_1$  and  $k_{-1}/k_L a_H$ :

*Table 1: Model Derived Rate Constants*

Temperature °C	$k_1$ (L/mol.s)	$k_{-1}/k_L a_H$
925	1.13E-03	1.05
900	8.16E-04	0.845
875	7.13E-04	1.41
825	4.50E-04	1.10
800	2.11E-04	1.31

The forward reaction rate constant goes up with temperature as it should. The negative natural logs of the forward rate constants,  $k_1$ , were plotted versus inverse temperature:

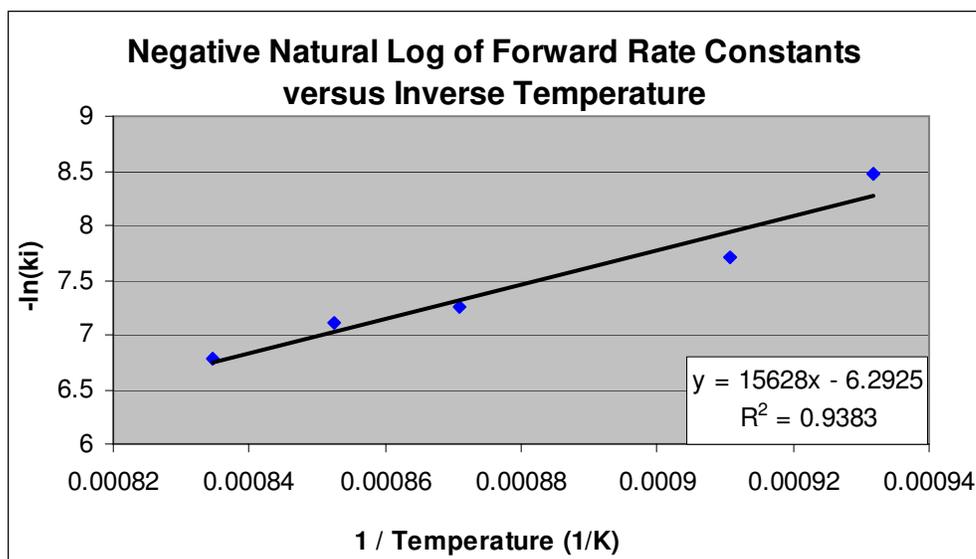


Figure 2: Determining the Arrhenius Rate Constants

As predicted, Figure 2 illustrates a straight line with an R-squared value of 0.94, which is very good for kinetic data. From the figure the following rate constant model was determined:

$$k = K \cdot \exp\left(-\frac{T^{\text{act}}}{T}\right)$$

where

$$K = 540 \frac{\text{L}}{\text{mol} \cdot \text{s}}$$

$$T^{\text{act}} = 15600 \text{ K}$$

or

$$E_a = 31 \frac{\text{KCal}}{\text{mole}}$$

This value for the activation temperature is very close to what Tran, et al [11] noticed: 31 Kcal/mole versus 35 Kcal/mole. This illustrates that using the reversible second order reaction, coupled with a mass transfer rate, actually does a good job of estimating the conversion of a sodium borate – sodium carbonate system where the carbon dioxide produced is not stripped using nitrogen.

Using the previous kinetic model for the forward rate constants, the second parameter, beta, was reevaluated for all runs. The following table shows the forward rate constants derived from the Arrhenius equation, the reevaluated beta constants, the residual sum of squares, and the residual standard deviation:

*Table 2: Reevaluated Model Rate Constants and Statistical Analysis*

Temperature °C	$k_1$	$k_{-1}/k_L a_H$	$S^2_{\text{residual}}$	$\sigma_{\text{residual}}$
925	1.17E-03	1.109	2.39E-03	0.0126
900	8.84E-04	1.121	9.37E-03	0.0235
875	6.62E-04	1.654	1.27E-02	0.0243
825	3.56E-04	0.975	1.83E-03	0.0107
800	2.55E-04	1.594	4.76E-03	0.0230

The second parameter,  $k_{-1}/k_L a_H$ , has a tendency towards decreasing as temperature increases. The negative reaction rate constant goes up exponentially with respect to temperature as does Henry's constant. The term,  $k_L a$ , also increases with temperature, but not exponentially. This would indicate that the  $k_L a_H$  term increases faster with temperature than the reverse reaction rate constant. The two data sets at 825°C did not correspond as well to each other unlike the other temperatures; this caused the  $k_{-1}/k_L a_H$  value to be less than the other temperatures.

The constants from Table 2 were used to create the following 6 figures:

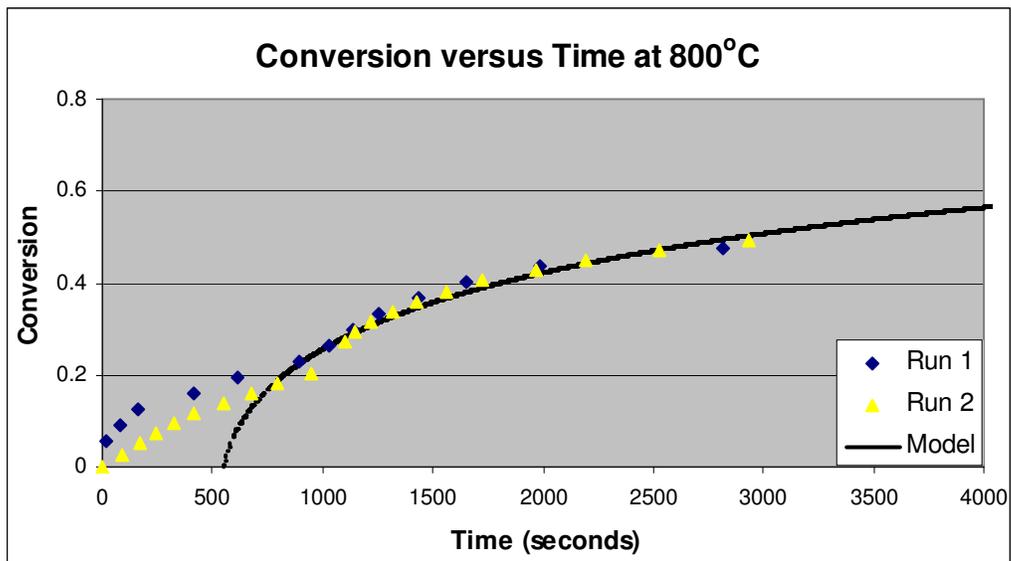


Figure 3: Model versus Experimental Data Conversion Times at 800°C

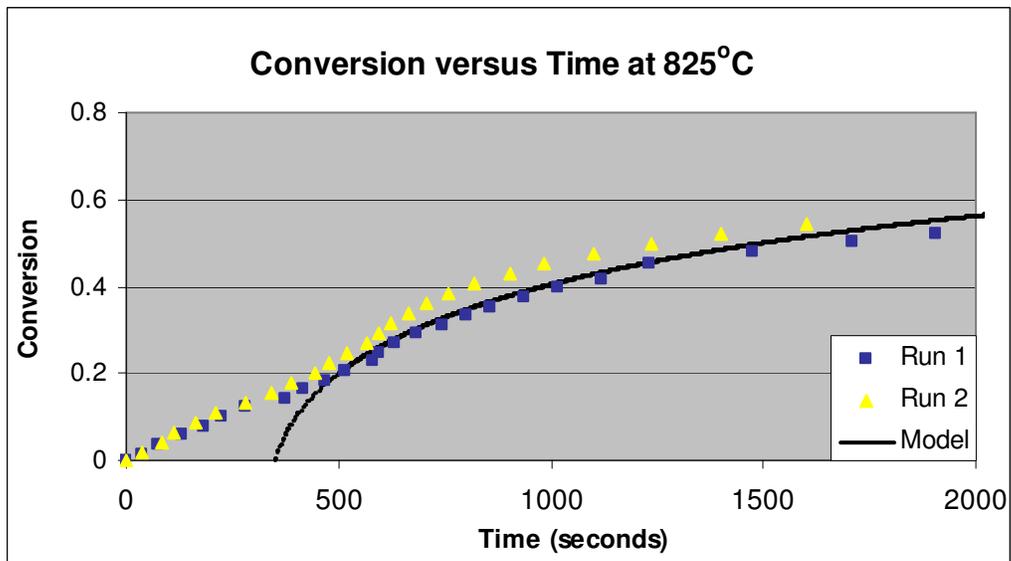


Figure 4: Model versus Experimental Data Conversion Times at 825°C

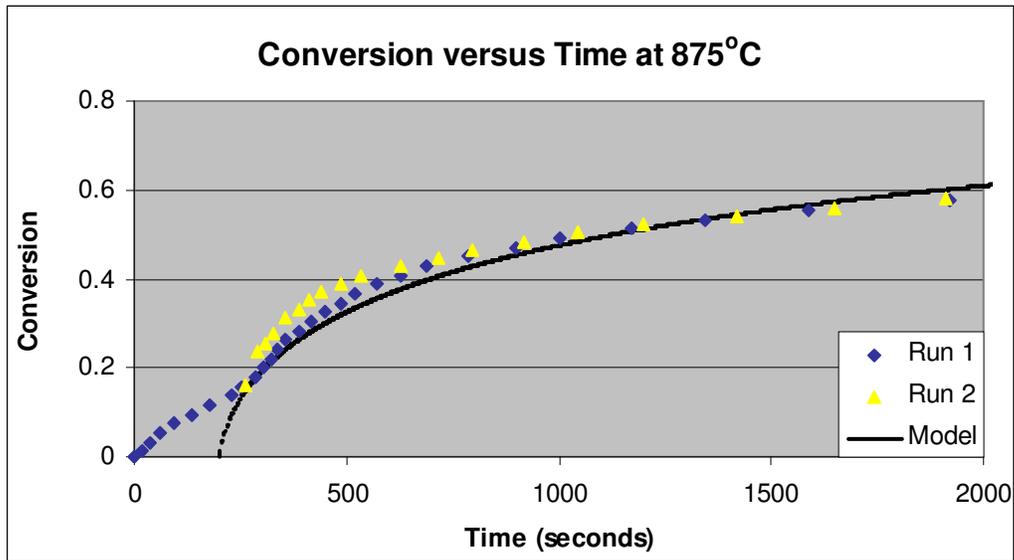


Figure 5: Model versus Experimental Data Conversion Times at 875°C

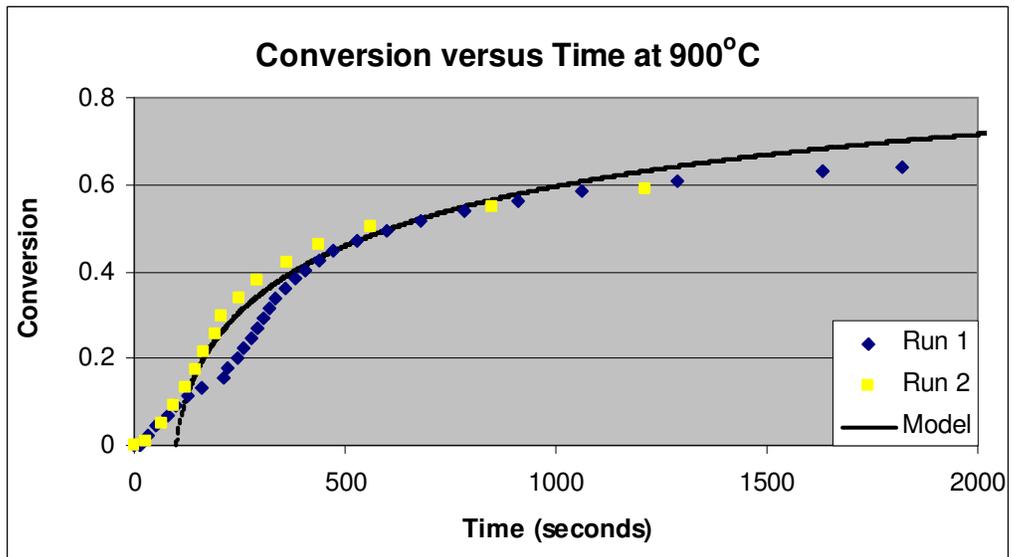


Figure 6: Model versus Experimental Data Conversion Times at 900°C

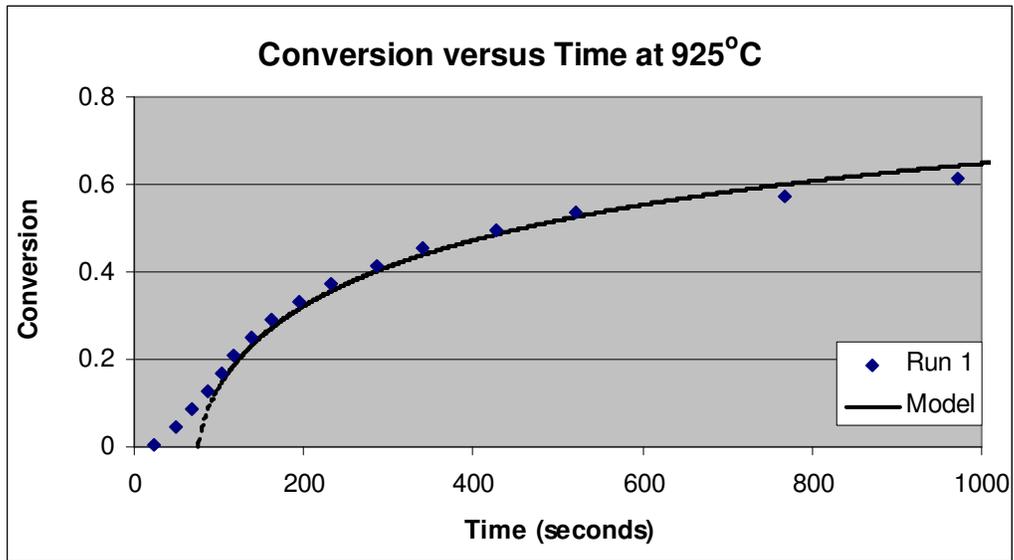


Figure 7: Model versus Experimental Data Conversion Times at 925°C

The model does a reasonable job of predicting the conversion using only two parameters, alpha and beta. The following figure illustrates the actual model versus time for various temperatures:

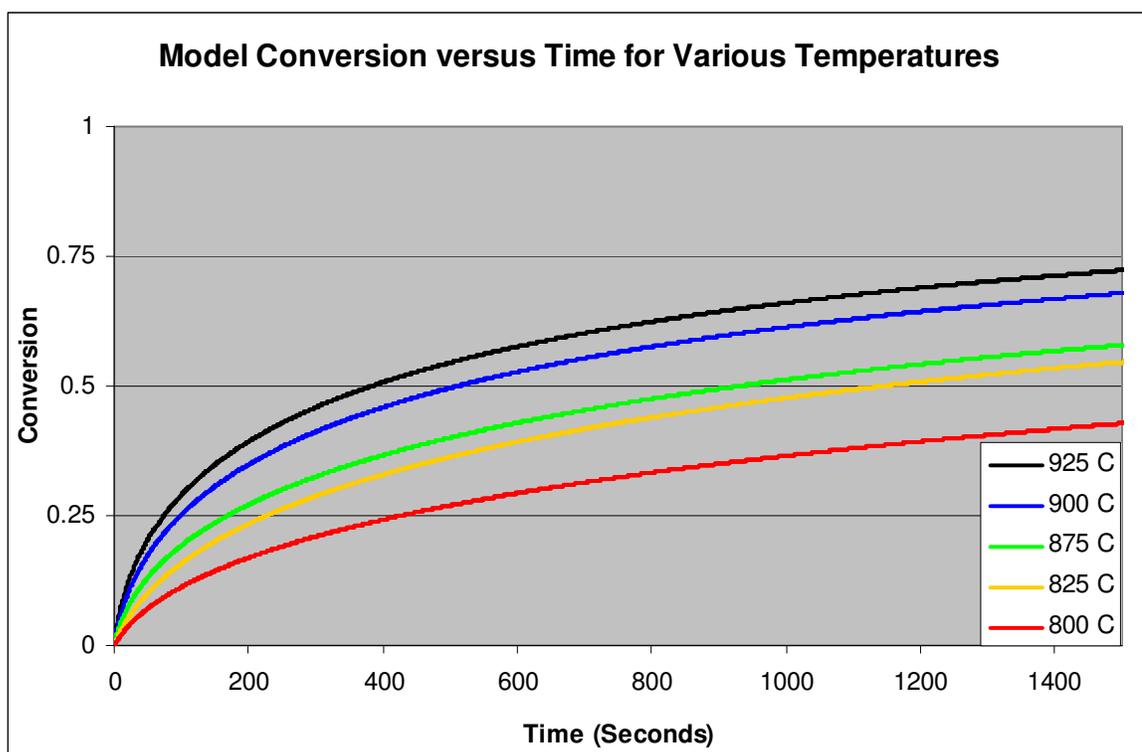


Figure 8: Model Conversion versus Time at Various Temperatures

### 6.3. Error Analysis

Table 2 lists the standard deviation between the model and the actual data points for the temperatures at which the experiments were run. However, it is quite difficult to visualize how good the model is compared to the data by just listing the average standard deviation. Instead, five plots were made where the actual values of conversion are plotted against the predicted conversion values made by the model. A perfect fit between the model and the data would yield a 45 degree line.

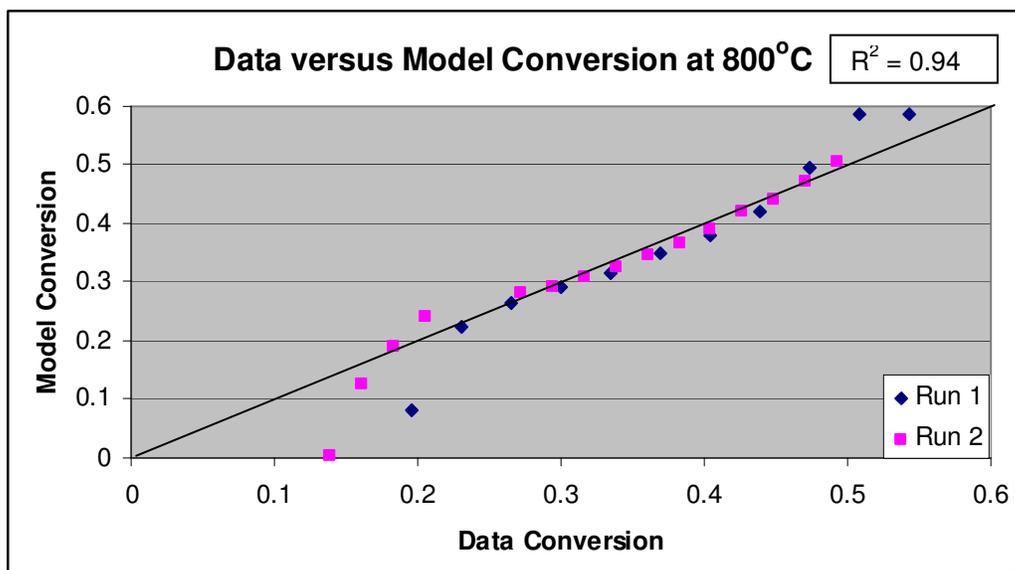


Figure 9: Data versus Model Conversion at 800°C

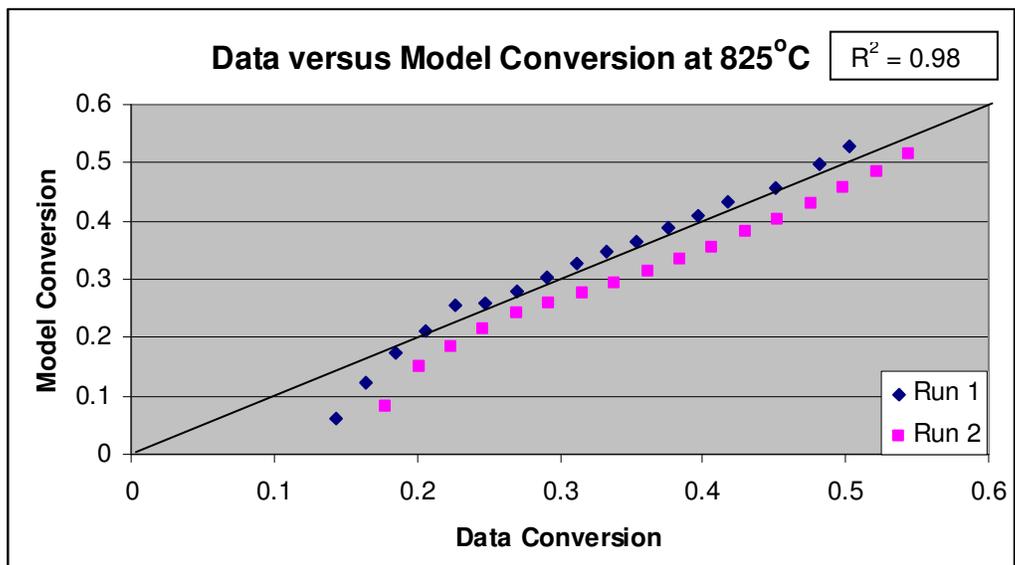


Figure 10: Data versus Model Conversion at 825°C

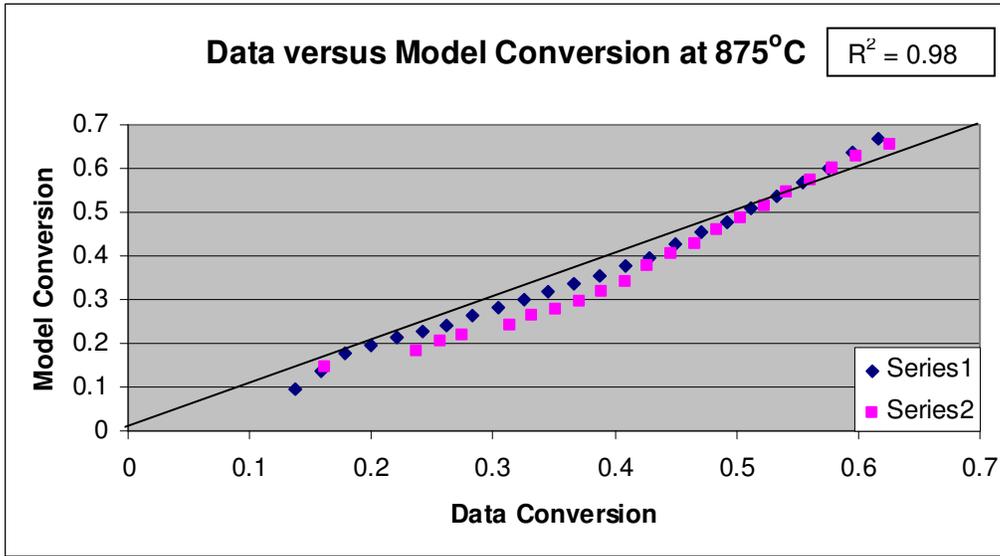


Figure 11: Data versus Model Conversion at 875°C

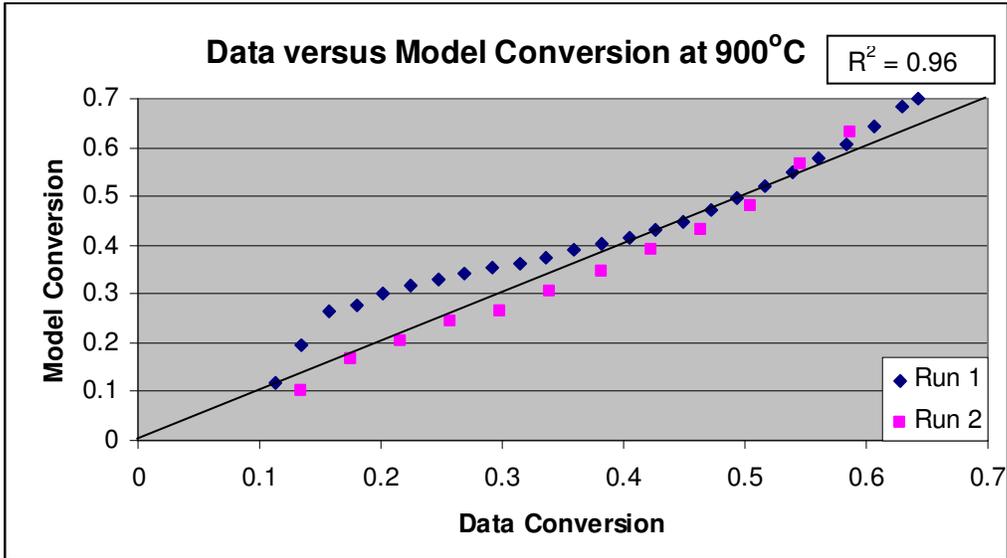


Figure 12: Data versus Model Conversion at 900°C

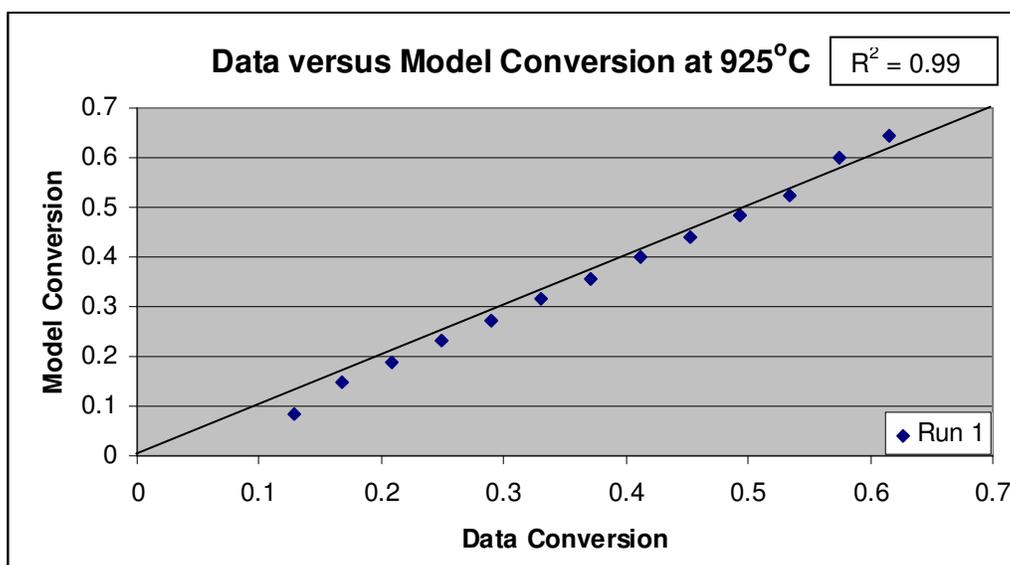


Figure 13: Data versus Model Conversion at 925°C

From Figures 9 through 13, it is shown that the model fits fairly accurately, with an average R-squared value of 0.97. Though there is a tendency for the model to underestimate the conversion during the beginning of the reaction and overestimating the conversion towards the end of the reaction. The tendency to underestimate in the beginning is probably associated with the experimental error that occurs fairly easily as the reaction rate is quite fast – once the rate slows down it is easier to follow the course of the reaction. This under estimation can also be due to the shift from a solid state to a liquid state, which is not modeled. Towards the end of the reaction, the model does not quite reach equilibrium as quickly as the reaction. At the equilibrium state the concentration of carbon dioxide in the smelt should be constant, however it takes longer for the model to reach equilibrium, which is probably due to the fact that it does not take into account the solubility of carbon dioxide in the liquid state.

## CHAPTER 7

### 7.1 Conclusion

Modeling the reaction between sodium borate and sodium carbonate proved to be rather difficult when the excess carbon dioxide was not stripped from the liquid system. Without removing the carbon dioxide, the equilibrium of the system shifted towards the reactants. This introduced a reversible term to the second order rate expression. However, the reverse reaction is a function of the two products, trisodium borate and dissolved carbon dioxide, which introduces the problem of the unknown amount of carbon dioxide in the liquid phase. Since, the conversion had been followed by the weight loss of the sample, which was characterized as the amount of carbon dioxide that left the liquid phase, a mass transfer rate had to be included. The mass transfer of carbon dioxide from the liquid phase to the gas phase could not be neglected as only some finite amount could leave at any given point. This leaves a small amount of carbon dioxide in the liquid phase that is freely available to revert back to sodium borate and sodium carbonate through the reaction with trisodium borate.

An expression for conversion was developed as a function of two parameters: one described by the forward rate constant and the other a ratio between the reverse rate constant to a mass transfer coefficient for carbon dioxide from the system. In order to solve the conversion expression, a marching-ahead approach together with a least squares analysis was used. This numerical approach gave reasonable values for the forward rate constant. The activation temperature was found to be 15600 Kelvin, which is an

activation energy of about 31 Kcal per mole. Previous research carried out by Tran, et al, listed their forward rate constant to be 35 Kcal per mole. It is quite good to be able to produce an activation energy so similar by two different methods: one by a simplified irreversible second order reaction –through stripping of carbon dioxide, and a second by a more complicated model that takes into account the mass transfer of carbon dioxide out of the liquid phase.

## **7.2. Recommendations**

One of the biggest issues with this study, was the problem of removing all of the water from the sample. Once the actual percentage of water in the sample was found, it was still difficult to get a good representation of the kinetic data as the weight loss was produced from both carbon dioxide and water leaving. For future projects I would strongly recommend using a online carbon dioxide analyzer and knowing exactly how much water is in the sample, so that a more accurate method of calculating the conversion could be used.

It would be interesting to figure out what the actual kinetics of the reverse reaction were. However, this would entail studying the vapor-liquid equilibrium of carbon dioxide with the smelt and estimating the mass transfer coefficient for the system. If one was able to get a value for the Henry's constant and the mass transfer coefficient as a function of temperature, then the reverse rate constant could be found. An alternative method could be to estimate the equilibrium constant of the sodium carbonate – sodium borate and carbon dioxide – trisodium borate reactions. Using this equilibrium constant

and the forward rate constants, the reverse rate constants can be found. This might be very interesting as the mass transfer rate of carbon dioxide could then be evaluated.

## APPENDIX

### Macro

Sub model925()

Dim C\_Conversion(500000)            'dimensionlizing the variables

Dim x(500000), time(500000)

For I = 0 To 35                    'Data collection from worksheet

    t = Cells((4 + I), 1)

    C\_Conversion(t) = Cells(4 + I, 2)

    time(t) = Cells((4 + I), 1)

Next I

    Abest = Cells(8, 8)            'best alpha parameter determined previously

    Bbest = Cells(9, 8)            'best beta parameter determine previously

    ntrials = Cells(5, 8)          'amount of iterations to be run

    bestss = Cells(11, 8)          'best s-squared found previously

    tstart = Cells(2, 8)            'time of start of reaction

    dt = Cells(4, 8)                'time increment

    ttotal = Cells(3, 8) / dt        'total amount of time increments

For nr = 1 To ntrials

    A = Abest + 0.0005 \* (0.5 - Rnd)    'random change in alpha

```

B = Bbest + 0.005 * (0.5 - Rnd)      'random change in beta

J = 0

x(tstart - dt) = 0                  'initial conversion

ss = 0                               's-squared set to 0

t = tstart

For n = tstart To ttotal              'loop to run reaction to completion

    x(n) = x(n - 1) + A * (1 - x(n - 1)) ^ 2 / (1 + B * x(n - 1)) * dt  'reaction

    t = t + dt                        'change in t

    t = Round(t, 2)                  'rounds time in case of computer error

Next n

    t = tstart

For n = tstart To ttotal

    ssnew = 0                        'sets s-squared to zero

    If time(t) = t Then              'compares model to data points

        ssnew = (C_Conversion(t) - x(n)) ^ 2          's-squared

    End If

    ss = ss + ssnew                  'sums individual s-squared

    t = t + dt

    t = Round(t, 2)

Next n

If ss < bestss Then                  'compares model s-squared to previous best

    bestss = ss                      'previous best becomes new s-squared if better

```

```

Abest = A          'previous best alpha becomes new alpha
Bbest = B          'previous best beta becomes new beta
Cells(8, 8) = Abest      'transfers numbers back to Excel Worksheet
Cells(9, 8) = Bbest
Cells(11, 8) = bestss
Cells(12, 8) = tstartbest

End If

Next

t = tstart

y = tstart

For n = tstart To ttotal

x(n) = x(n - 1) + A * (1 - x(n - 1)) ^ 2 / (1 + B * x(n - 1)) * dt 'reaction

If y = t Then          'transfers every 10 seconds of data to Worksheet

    Cells(3 + J, 6) = x(n)

    Cells(3 + J, 5) = t

    J = J + 1

    y = y + 10

End If

t = t + dt

t = Round(t, 2)

Next n

End Sub

```

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