Application of Differential Scanning Calorimetry to Characterize Thin Film Deposition Processes

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APPLICATION OF DIFFERENTIAL SCANNING CALORIMETRY TO
CHARACTERIZE THIN FILM DEPOSITION PROCESSES

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DEDICATION

I’d like to dedicate this thesis to my family. My father, mother, and brother have supported me through my undergraduate and graduate careers. Thanks for the love and support letting me travel away from home to earn a great education and meet wonderful new friends.
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ABSTRACT

With the recent increase in awareness on the environmental impact of industrial coating processes, chromate-based coating processes have been elevated to the rank of the technologies targeted by the EPA for rapid replacement by environmentally friendly processes. Therefore, there is a clear need for advances in coating technologies to identify alternative industrial practices.

This thesis characterizes a process developed at Cleveland State University as an alternative deposition technique to generate uniform coatings onto solid substrates. A kinetic analysis to extract scale up parameters involved in the reaction kinetics leading to high-performance coatings is demonstrated in this research. The work consists of thermal characterization of deposition experiments using Modulated Differential Scanning Calorimeter (MDSC), complemented with preliminary finite-element-modeling (FEM) of fluid flow and transport phenomena in the vicinity of the deposition assembly.

MDSC is capable of using linear and modulated heating rates. Modulation over imposes a sinusoidal heating profile to a linear heating rate. Therefore, modulation combines two conventional DSC experiments into one. Modulation provides the ability to
differentiate reversibility from irreversibility in transitions. This study intends to study both the advantages and disadvantages of the modulation compared to conventional DSC in the analysis of thin film deposition.

A protocol to analyze deposition reaction kinetics using a conventional DSC was formulated in this research. While modulation was unable to produce results that could be compared to the conventional DSC, further in-depth studies need to be completed. This research outlines the experimental procedure to analyze deposition reactions via conventional DSC, and a kinetic analysis procedure to extract reaction kinetics is demonstrated.

This research successfully demonstrated that the deposition mechanism can be characterized via DSC experiments. Further studies are anticipated to lead to scale-up criteria and detailed kinetic characterization of coating technologies leading to conversion and protective coatings.
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CHAPTER I

INTRODUCTION

Metal surface treatment processes have been successfully used for decades; however, there are concerns about the environmental impact of these processes. Acids and chromates generate large amounts of wastewater resulting in serious environmental problems. The hexavalent chromium-ion containing solid waste is increasingly difficult and costly to dispose off (Chang et al., 1997).

The Environmental Protection Agency (EPA) of the United States and Health Agency of United Nations all restrict the usage of chromate-containing chemicals and plan to totally eliminate them in a few years. Therefore, there is a clear need for new advances in coating technology to identify alternatives to present industrial practices (Chang et al., 1997).

Hanyaloglu studied the use of tri-cresyl phosphate (TCP). The ortho-isomer of TCP has been found to be an active neurotoxic agent in a report supplied by the National Institutes of Health (NIH) and the International Programme on Chemical Safety (Rao, 1993). The usage of TCP has significantly been dropped. TCP has been replaced by safer phosphate esters such as tert-butylated triphenyl phosphate (TBTPP). In previous research,
TBTPP has been shown to successfully promote thin films on iron containing surfaces (Morales et al., 2000).

Nagarajan developed a model of the film deposition process incorporating transport and kinetic parameters that match experimental data of TBTPP (Nagarajan et al., 2006). The model uses a modified thermal gravimetric analyzer (TGA) to study the Chemical Vapor Deposition (CVD) mechanism for wear and friction control on iron-based alloys. Using pseudo-steady state to analyze the mass transfer through the film, Nagarajan concluded the reaction mechanism consisted of a kinetically controlled region and a combination of kinetically and diffusive controlled region. The previous research created thick films and observed that thin films will be deposited in the kinetically controlled reaction mechanism region.

In this research, TBTPP is combined with an iron additive to allow for thin films to be grown on any substrate regardless of the composition. Anhydrous Iron (II) Acetate is the selected iron additive to be combined with TBTPP to form a homogeneous solution. The iron additive allows the lubricant to deposit on any substrate.

This research targets the development of thin films produced in the kinetically controlled region of the reaction mechanism by a Chemical Vapor Deposition technique. The reaction mechanism is driven by the surface reaction between the solution and surface. This region is non-isothermal and the relationship between temperature and the surface reaction needs to be characterized. Differential Scanning Calorimetry (DSC) is used to perform thermal analysis on the solution of TBTPP and iron (II) acetate. DSC measures the heat flow of a sample versus the temperature and time.
DSC experimental data will allow kinetic analysis to be performed by characterizing the surface reaction that forms thin films. The analysis will use batch reactor design equations to extract important reaction kinetic parameters: activation energy, reaction order, and reaction rate constant. Using these parameters a model will be developed through finite element modeling to simulate a laboratory-scale furnace.

Numerical simulation is an important development to experimental design. Simulation reduces the amount of experiments required. The kinetic parameters are used in designing a simulation of a laboratory scaled furnace. The simulation uses transport effects, concentration effects, thermal profiles, and reaction kinetics to develop a model of the furnace. Simulation can identify difficult areas of analysis for future experiments. The numerical simulation results can be compared to real laboratory scaled results to check for accuracy and reproducibility.

After coatings have been created tests can be performed to identify the properties and applicability of the films. Two tests have been explored in previous studies: Tape Adhesion Testing and 24-Hour Corrosion Testing. These tests explore the physical and chemical properties of the films. The ability to corrode and protection strength are two very important qualities in protective coatings.

1.1 Statement of the Problem
Existing applications of chromate-based coating processes are in the aerospace, automotive, and the construction industries (Reye et al., 2004). Some specific examples of chromate-based processes are lubrication and paint priming. Coatings provide enhanced properties to protect from different degradations or enhance specific properties. Corrosion resistance and adhesion enhancement are two examples of protective coating properties.
The hexavalent chromium-ion containing solid waste is dangerous and increasingly difficult and costly to dispose of. This environmental cleanup and health hazard is a reason to replace chromium based processes. In order to replace chromate-based coatings, a feasible replacement needs to possess equivalent properties of corrosion resistance and adhesion enhancements (Reye et al., 2004). The properties of potential replacements need to be characterized and optimized to compare against the hazardous chromium processes. Ester phosphates have been proposed to potentially replace chromium processes.

This research focuses on characterization of the environmentally friendly metal-working fluid (ester phosphates) to create protective coatings via a Chemical Vapor Deposition technique. The research focuses on the reaction kinetics detected when using Chemical Vapor Deposition to create thin film coatings with solutions of ester phosphates and iron (II) acetate as precursors.

Chemical Vapor Deposition (CVD) is a common technique used for depositing uniform coatings on solid substrates. CVD has been used in a variety of different applications such as insulation, creating protective coatings, and synthesis of advanced materials. CVD has many uses, but is also very complicated. CVD constitutes an important technology for the manufacturing of thin solid films, i.e. in semiconductors and solar cells, as antireflection and spectrally selective coatings on optical components (Kleign et al., 2007). CVD requires the combination of chemical thermodynamics, kinetics, and transport phenomena. CVD has the potential to create uniform coatings on unique geometries, making it a useful technique.

Thin film processes are thermally analyzed based on the scope of the research. To
achieve an analysis of the deposition rate, a Thermo-Gravimetric Analyzer (TGA) was used. The TGA measures the weight of the sample while it is being heated or cooled (Nagarajan et al., 2006). This provides isothermal experiments that measure the amount of deposition occurring. Activation energy can be extracted from experimental data provided multiple different temperature experiments are conducted.

The CVD technique used in the current research requires a reaction to deposit on the substrate. This reaction is analyzed to extract reaction kinetic parameters for future development. To extract these parameters, an analysis of heat flow is required. The Differential Scanning Calorimeter (DSC) records heat flow versus time and temperature. The DSC is the main experimental equipment used in this study to characterize thin film processes. The DSC has two capabilities for thermal analysis: (i) Conventional DSC heating profile applies a linear temperature profile during experiments and (ii) Modulated DSC heating profile applies a linear temperature profile overlaid with a fluctuating sinusoidal temperature profile.

An additional technique to analyze thin film processes is to use laboratory scaled experiments and test the coatings created for specific properties and compositions. The films created can be characterized by X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) (Reye et al., 2004). These techniques show the composition of the films and their corresponding percentages. The films can also be tested for their adhesion properties and corrosion resistance properties.

Current research explores the reaction kinetic parameters of the CVD reaction through conventional DSC and modulated DSC techniques. These parameters will lead to
the ability to properly scale up the process using the environmentally friendly ester phosphate to potentially an industrial scaled process. The advantage of using the DSC is to create a controlled environment where the reaction can be properly analyzed and replicated. This environment supports an accurate analysis of heat flow versus temperature and time. Disadvantages using the DSC can be the inability to detect the CVD reaction. This disadvantage may be attributed to non-homogeneous solutions, inert gas flow-rate releasing excess reactants, or improper temperature profiles.

1.2 Literature Survey

1.2.1 Environmental Awareness

A significant amount of work has been done pertaining to the development of chromate conversion coatings. If it were not for the issue of toxicity, hexavalent chromate coatings would still be widely used today. Though chromate coatings have been commonly used with aluminum, a number of other metals and their alloys can also be treated (e.g. cadmium, copper, magnesium, silver, and zinc). Chromate conversion coatings are produced on various metals by chemical or electrochemical treatment with mixtures of hexavalent chromium and certain other compounds. These coatings convert the metal surface to a superficial layer consisting of a mixture of chromium compounds. The coatings are usually applied by immersion, although spraying, brushing, swabbing, or electrolytic methods are also used (Eppensteiner et al., 1999). Besides chromate coatings, various phosphate coatings have been used with aluminum. Bibber wrote an article giving the reader an overview of hexavalent and non-hexavalent chromium conversion coatings (Bibber, 2001). The article also explains some of the issues involving
generating conversion coatings on aluminum, which include a discussion on both chromate and phosphate coatings.

Chromate-based paints containing Chromium (VI) are applied as a first-coat primer onto metals to protect them from corrosion damage (Sabty-Daily et al., 2005). Chromate containing spray paints are widely used in the aerospace industry and expose workers to dangerous Cr(VI). Cr(VI) poses a significant risk of cancer to the respiratory system, has been classified a group 1 carcinogen by the International Agency of Research on Cancer, and as a group A carcinogen by the U.S. Environmental Protection Agency (Sabty-Daily et al., 2005).

Sabty-Daily assessed the size distribution and speciation of Cr in paint spray aerosol in two field studies at an aerospace manufacturing facility, to evaluate whether reduction of Cr(VI) in paint aerosol samples occurs and whether any reduction is dependent on particle size, and to estimate the fraction of Cr(VI) deposited in the head airways, tracheobronchial and alveolar regions based on Cr aerosol size distributions (Sabty-Daily et al., 2005).

Sabty-Daily concluded in the study, that the mass of total Cr and Cr(VI) in paint aerosol samples of two field studies consisted primarily of particles > 10 µm. Seventy-two percent of Cr(VI) mass in paint spray aerosol potentially inhaled by a spray painter may deposit in the head airways region (Sabty-Daily et al., 2005). This is a significant conclusion of the occupational hazard operating chromate based spray paints.

Zinc chromate is one of the anticorrosive pigments most frequently used in the formation of primers (Bethencourt et al., 2003). However, its aggressiveness and toxicity
severely restricts its use, shown by Bethencourt environmentally friendly alternatives are explored in order to replace zinc chromate (Bethencourt et al., 2003). Red lead and zinc chromate are highly toxic and cause serious environmental pollution. Zinc phosphate and second generation pigments have been proposed to replace the dangerous compounds (Bethencourt et al., 2003). By studying the inhibitor properties in neutral, basic, and acidic extracts, the zinc chromate increases the corrosion rate of the carbon steel studied in an acid medium. This study concludes that the zinc phosphate and alternative second-generation zinc phosphate pigments are more effective in acid media than zinc chromate (Bethencourt et al., 2003).

1.2.2 Chemical Vapor Deposition

Various works have generated phosphate films on aluminum. Surface studies of phosphate deposition onto bearing steel were done at the Air Force Research Laboratory at Wright-Patterson Air Force Base. Foster performed various spectroscopic analyses on depositions of tertiary-butyl phenyl phosphate. Infrared bands consistent with inorganic poly-phosphates and phosphites were detected in the deposition films generated from the tertiary-butyl phenyl phosphate (Forster, 1999).

In another work, Forster combines kinetic and diffusion phenomena in an analysis to estimate diffusion mechanisms for iron and carbon in the vapor phase lubrication of bearing steel (Forster, 1999). By ignoring the decomposition and kinetics of the phosphate ester, Forster assumed the diffusion mechanism to control the deposition process. Using Auger depth profiles of the bearing steel, diffusion parameters were estimated. Results showed that the diffusion occurs by way of iron cation migration through an anionic lattice of polyphosphate and phosphite.
Forster continues by proposing a mechanism that explains many of the decomposition products and the formation of a bound glassy iron phosphate film by characterizing the films deposited by TCP and tertiary-butyl phenyl phosphate (Forster et al., 2002). Forster examines films through Auger spectroscopy suggesting iron phosphate as the film. Also, Forster through x-ray photoelectron spectroscopy shows the presence of a bound organic layer at the surface. Forster uses TCP despite some recognized problems such as hydrolysis and neurotoxicity because of their commercial importance due to their stability, high ignition temperature, low heats of combustion, and boundary lubrication characteristics (Forster et al., 2002).

Forster forms a lubricious film at temperatures of 800°C in a nitrogen atmosphere and 550°C in air. This poses the possibility of the gaseous environment affecting the CVD mechanism. Forster concludes the phosphate esters degrade via different pathways. In the presence of the metal the products depend on the availability of oxygen at the metal surface (Forster et al., 2002). When oxygen is plentiful, cresol is the primary product. If there is less oxygen available additional products such as tolyl-TCP are formed. Forster showed that further reactions leads to the formation of fused-ring aromatic compounds (Forster et al., 2002).

In a different study, Kok looked to identify conditions that grew small, strongly adhered zinc phosphate crystals onto Al-6061 alloy resulting in high coverage and uniform conversion coating (Kok et al., 2001). Low zinc solutions provided a higher coating coverage using a fluoride-etching additive at various solution concentrations. To deviate from chromate and phosphate coatings, work was done to characterize a zinc-aluminum phosphate catalyst (Mtalsi et al, 2001). What is useful about the paper is the
degree of characterization done in this work. Characterization was done by nitrogen adsorption-desorption, x-ray diffraction, Fourier transform infrared spectroscopy, Thermo-gravimetric analysis, differential thermal analysis, diffuse reflectance infrared Fourier transform infrared spectroscopy, and temperature programmed desorption of ammonia. The catalyst is a phosphate-based structure analyzed by some of the techniques described later in this paper.

Sanchez studied the chemical vapor deposition of aluminum on ferritic steel in a fluidized bed reactor. A thermodynamic study of the partial pressures of the gaseous species in the system during CVD has been performed using Thermocalc software (Sanchez et al., 2007). The coating obtained has been tested by XRD, SEM, EDX and the optimum input ratio of the gas was obtained. This study varies the active HCL gas input ratio (in volume) and the time allotted for deposition. The thermodynamic software optimizes the operation temperature and input gas ratio.

This study suggests a different form of CVD compared to the current study. The reactive gas is inputted through the reactor picking up aluminum to react and then deposit on the substrate. In fluidized bed reactors the particles behave like liquids when the gas is fed through the bed (Sanchez et al., 2007). The coating deposited is an iron-aluminide inter-metallic diffusion coating effect for improvement in oxidation and corrosion resistance at high temperatures.

Shown in this alternative application of CVD, the thickness of the coating is dependent on the input ratio of reactive gas. When the HCL input ratio is increased, the precursors partial pressure, involved in the reaction, also increases and therefore the
coated specimen mass gain is thicker. Coatings were created from 0.5 to 11.0 µm (Sanchez et al., 2007). The growth of the coating is controlled both by diffusion and reaction processes. At short deposition times the growth is governed by chemical reaction, but when deposition time is higher the growth control is by diffusion processes.

Zhang studied a laboratory CVD technique to control the coating’s composition, purity, and microstructure. Temperature, Aluminum activity, and post-aluminizing anneal on the coating growth was investigated (Zhang et al., 2008). These coatings were observed on iron containing alloys compared with nickel alloys. This study shows the ability to control the exact composition of coatings allowing a unique coating to be deposited upon desired command.

Zhang showed the coating thickness of the outer layer being controlled by the aluminum activity in the CVD process. The thicker coatings formed in the “high-Aluminum” process on the austenitic alloy tended to spall due to the mismatch between coating and substrate (Zhang et al., 2008). Based on the composition and microstructure, the coating growth is likely a combination of outward diffusion of Iron and inward diffusion of Aluminum (Zhang et al., 2008). This combination once characterized can be shown to control the composition and microstructure of created deposition coatings.

Zhang, Pint, Cooley, and Haynes review the advancement over the decades of the CVD reactors and the progress that still needs to be made to completely characterize CVD reactors. A new challenge that needs to be explored is the atomic layer deposition that is a transient process (Zhang et al., 2008). The next step in CVD modeling is
progressing towards atomic and crystal grain scale influence on the functional properties of the film.

Kleign described the multi-scale simulations of CVD processes and equipment over the past decades. The CVD process has been researched and published since the 1970s. With the development of computers, simulations have greatly increased the characterization and designing of CVD mechanisms (Kleign et al., 2007). Today’s engineers have the ability to routinely use simulation models for specific processes using commercial software codes.

Recent advancements of computer processing relates directly to the advancement of computer modeling of CVD mechanisms. In the last decade the integration of reactor scale, multi-dimensional transport models, and detailed chemistry models have been employed (Kleign et al., 2007). This advancement advances the development and operation of CVD reactors, but also advanced the way CVD researchers conceptualize the processes in the CVD reactors.

1.2.3 Alternative Deposition techniques

Wang and Liu explored the use of solid lubricants creating almost fully dense self-lubricating composites. The composites consist of a matrix phase interpenetrating through the microstructure at a specific temperature creating a self-lubricating composite (Wang et al., 2008). This work represents a new approach in producing self-lubrication metal ceramic composites with an interpenetrating network. Molten solid lubricant flows through the micro-pores similar to sweat glands in a human. Wang and Liu explore the feasibility of achieving low friction coefficients and low wear at high temperature in the self-lubrication metal ceramic composites with an interpenetrating network, the
evaluation of friction and wear characteristics of the newly formed materials and the mechanisms of transfer film formation in these self-lubricated composites (Wang et al., 2008).

Wang and Liu showed that it is to infiltrate Pb-Sn based solid lubricants into porous metal ceramic composite pre-forms to fabricate dense and homogeneous self-lubrication composites with interpenetrating network (Wang et al., 2008). The resultant composite has good mechanical properties as well as perfect tribological properties. Wang and Liu conclude by adding 15% silver in mass the sliding friction behavior of the composite upper 400°C can be improved distinctly, especially under high loads (Wang, et al., 2008). This research provides an alternative lubrication technique that is researched and analyzed to characterize thin film protective coatings or lubrication layers.

Goto explored high speed deposition films by conventional thermal CVD and Plasma-Enhanced CVD (PE-CVD). A Laser CVD (LCVD) process has been recently developed attaining an extremely high deposition rate of 660 μm/h (Goto, 2004). Plasma emerged during the last CVD and is explored. By accelerating the flow rates the deposition rate can be characterized and is shown through the high deposition rate of laser CVD (Goto, 2004).

Goto showed that accelerating the deposition rate is an important issue. Optimizing CVD a high deposition rate consists of 100 μm/h (Goto, 2004). The laser process significantly increases this deposition rate and explores the emergence of this new process. This new process could be laser-induced plasma CVD, not a line of sight
process, and suitable for coating on complicated components such as turbine blades (Goto, 2004).

### 1.2.4 Computer Simulations of Deposition Techniques

Danielsson formulated a 3D simulation of a silicon carbide CVD reactor, including inductive heating and fluid dynamics as well as gas phase and surface chemistry (Danielsson et al., 2002). The simulated results have correlated well to experimental data. These simulations involve the growth of depositions in a horizontal hot-wall CVD reactor operating at 1600°C, applicable to any reactor configuration because no adjustable parameters were used in fitting the experimental data (Danielsson et al., 2002).

Danielsson developed a model for the epitaxial growth of SiC. The growth has been found limited by mass through the transport of the film to the surface. To increase the accuracy of the model, the molecular properties, i.e. the Lennard-Jones parameters, are necessary (Danielsson et al., 2002). The simulation results have been compared to a small scale experimental reactor, but because no adjustable parameters have been used to fit experimental data, the reactor can be adjusted to fit the needs of the researcher.

Choo and Adomaitis address the limitations of spatial actuation and sensing capabilities necessary to control deposition uniformity, or to intentionally induce non-uniform deposition patterns for single-wafer CVD experiments (Choo et al., 2005). A CVD reactor system has been developed by Choo and Adomaitis that can explicitly control the spatial profile of gas-phase chemical composition across the wafer surface. Simulations based designs and experimental results are compared for tungsten films.
Using the constructed CVD reactor systems it is shown that the composition and uniformity or non-uniformity can be controlled. This spatially controlled CVD reactor opens the door to a new generation of CVD reactor designs, allowing single-wafer combinatorial studies and precise across-wafer uniformity control in a single reactor design (Choo et al., 2005).

1.2.5 DSC Capabilities and Technological Advancements

Pistofidis characterized the reaction mechanism of zinc pack coatings up to 550°C using a DSC (Pistofidis et al., 2006). The complete reaction mechanism of zinc pack coatings is known and able to be detected using the DSC. Coatings observed from the zinc pack occur in three steps: transformation of intermediates, formation of salts, and the deposition of films (Pistofidis et al., 2006). By knowing the mechanism to create coatings, the DSC can clearly observe the thermal transformations. Unknown reaction mechanisms are only able to theorize when a transformation occurs. When the reaction mechanism is determined the thermal analysis will readily identify each transformation.

Wada explored another capability of the DSC, sulfidation reaction. Sulfidation reaction is the reaction between and element and sulfur to create sulfides. The reaction kinetics of sulfidation is not well known and needs to be properly researched (Wada et al., 2004). To study the kinetics of sulfidation, Wada used the DSC to perform analysis. Multiple different elements are tested. This analysis exhibits the wide range of analysis that the DSC is capable of performing. The reaction kinetics are shown to be studied for sulfidation reaction and the current research studies the reaction kinetics of CVD reactions.
Danley utilized the MDSC’s ability to separate the sample heat flows resulting from time dependent and time independent processes (Danley, 2003). Danley showed MDSC has been hampered by the inability to obtain high quality results at short modulation periods. Heat capacity measured by MDSC should be independent of the period of modulation and indeed that is the case for sufficiently long periods (Danley, 2003). Danley showed a large part of this period dependence is due to instrumental effects and may be eliminated by applying the MDSC heat flow calculation method described by Danley. The TA Instruments Q1000 DSC includes two differential temperature measurements and is constructed such that mutual heat exchange between the sample and reference calorimeters is virtually eliminated it is capable of measuring the sample and reference heat flow rates independently (Danley, 2003), a necessary condition for application for the method described by Danley. Danley also concluded that the sample thermal diffusivity may also cause a period dependence (Danley, 2003). By preparing a thin, flat sample may avoid such problems.

A common analysis requires the use of a DSC, TMA, and FTIRS, but is unable to correlate a real time analysis of these three different tests. Degamber reported a novel technique which combined DSC, FTIRS with a non-contact fibre optic thermal expansion probe to give simultaneous thermal, spectral, and dilatometric information on a polymer sample (Degamber et al., 2004). Degamber constructed a prototype tool and provided experimental data proving the accuracy of the new technology (Degamber et al., 2004). This ability allows a complete analysis of composition, thickness, and reaction kinetics to be detected and monitored in real time.
Current research would benefit from the combined technology presented by Degamber. This technology allows for complete real time comparable data of experiments. Different experiments possible will not portray comparable trends, leading to contradictory results. Degamber prototype results shows that this technique can be readily and successfully implemented to study in real time the thermal, spectral and dilatometric properties of a material as it undergoes a transition (Degamber et al., 2004).
CHAPTER II

EXPERIMENTAL

2.1 Preparation of the solutions

The major component of the solution is a tert-butylated triphenyl phosphate (TBTPP), commercialized as Durad 620B. TBTPP has been shown to successfully promote thin films on iron containing surfaces (Morales et al., 2000). In this research, TBTPP is to be combined with an iron additive to allow for thin films to be grown on non-iron based surfaces. Anhydrous Iron (II) Acetate was the selected iron additive to be combined with TBTPP to form a solution that has the ability to be a precursor for thin films. Iron (II) acetate not only contains a transition metal, but it is the only additive found to form solutions TBTPP (Reye et al., 2004).

Previous research suggests that only certain ratios of anhydrous iron (II) acetate additive to TBTPP will yield stable of solutions (Reye et al., 2004). The goal of this protocol is to create a homogeneous solution of TBTPP and the additive that almost replicates the structure of pure TBTPP. Excessive additive has shown to lead to sedimentation of the iron (II) acetate. While too dilute, solutions might be unable to promote the deposition of thin films on the substrates used in this research. In the absence of solubility data, a parametric study was completed to test certain molar ratio solutions
to be dilute, soluble, or supersaturated (Reye et al., 2004). Appendix D shows the different combinations used to formulate testing solutions (see Appendix D). In this research a 2.5% molar solution was selected as a case-study. This solution was selected because upon preliminary studies, the reaction was consistently shown by a 2.5% molar solution.

Similarly to other commercial lubricants, TBTPP is highly viscous and difficult to combine into a homogeneous solution with solid additives. Iron (II) acetate is a solid powder that is soluble in water and other polar solvents. Previous research suggests using methanol as the solvent to promote a homogeneous mixture (Reye et al., 2004). The introduction of methanol provides a substance that both TBTPP and iron (II) acetate are soluble in. Methanol has been chosen because of its low boiling point (64.7°C) and at standard conditions high volatility, (Vapor pressure is 12.8 kPa @ 20°C), and wide availability. Other solvents tested were ethanol and water but each of these solvents require heating to separate from the mixture. This research studies the heating effects on the solution and in order to prevent heating effects prior to analysis, this heating is avoided. The combination of low boiling point and high volatility allows for methanol to create a soluble, homogeneous solution with TBTPP and iron (II) acetate and then easily be evaporated out of the solution leaving a soluble homogeneous mixture of TBTPP and iron (II) acetate.

Despite the low boiling point of methanol, the lab temperature is still below this temperature. To speed up the evaporation of methanol from solution while avoiding heating the solution, a vacuum apparatus is implemented to lower the boiling point of methanol further. This vacuum prevents the use of heating the solution to evaporate the
solvent out. If a different solvent such as ethanol or water were used, heating the solution would be necessary to evaporate the solvents out. Heating the solution is avoided because thermal analysis will be performed on the final solution to extract important kinetic parameters. If the solution was heated, some solution may be carried out of solution or affected by the heating effects. To reduce such error that may occur, the vacuum system is applied to remove the solvent at room temperature without heating effects.

Figure 1: Schematic of Vacuum Apparatus

Shown in the figure 1 is a vacuum system consisting of a simple magnetic stirrer inside of a vented Erlenmeyer flask to induce a homogeneous mixture. The Erlenmeyer flask is vented to a water faucet aspirator that creates a slight vacuum system in the topped Erlenmeyer flask. The aspirator used in the lab is advertised to achieve an ultimate vacuum of 724 torr.

The samples consisted of 25 mL vials of TBTPP and Iron (II) Acetate solutions. Iron (II) acetate is delivered as an anhydrous powder packed under Argon gas because of its high reactivity in the presence of oxygen and its high tendency to absorb water;
therefore, any exposure to the humidity is to be avoided as much as possible to prevent water from reacting with the anhydrous powder. This powder is combined in a small amount with TBTPP allowing for the assumption that iron (II) acetate occupies a negligible volume in the total solution.

Using this assumption, the 25 mL solution requires 25 mL TBTPP and the corresponding amount of additive to create a 2.5% molar solution. These two substances are now combined in the Erlenmeyer flask. Methanol is now used in excess to induce proper mixing and promote homogeneity. The flask is now connected to the vacuum system to induce the vaporization of methanol, yielding a homogeneous solution in approximately a week. The calculations of this sample preparation can be viewed in Appendix D.

2.2 Testing the Solutions

As the solution changes color into a darker brownish red, contamination tests need to be performed to check the degree of evaporation of methanol. If a final solution contains methanol the thermal analysis of the thin films will be tainted because of the excess reactant taking up volume and mass. A sample is taken and used to perform a simple experiment with the DSC. This experiment consists of a simple heating ramp from ambient temperature to 100°C. This heating ramp covers the area of methanol’s boiling point (64.7°C). Figure 2 reveals a large peak identifying the remnants of methanol still in the solution.
Figure 2: Experiment with methanol contamination

The longer the solution remains in the vacuum apparatus the methanol peaks diminish and eventually show a contaminant free molar solution of 2.5% iron (II) acetate and TBTPP.

After approximately a week, the solution will be homogeneous and ready for experimentation and analysis. The tests for methanol will not reveal any methanol peak reaffirming the fact of complete vaporization of the polar solvent from the solution has occurred. The solution is now a homogeneous mixture of TBTPP and iron (II) acetate.

2.3 DSC Tests for Optimum Kinetic Analysis Conditions

2.3.1 DSC

Two differential scanning calorimeters (DSC) can be used to conduct thermal analysis for the micro-scale experiments. A Du Pont Instruments 912 DSC, consisting of a basic ambient pressure cell that has the ability to control the temperature profile while
recording heat flow. Two thermocouples placed under the reference and sample pans measure the heat difference between these two pans. Placed on top of the thermocouples, hermetically sealed pans are used to contain samples. The pans and pinhole lids are common for both DSCs. The Du Pont Instrument uses a TPI-TA Temperature Programmer Interface to connect the DSC to the data-acquisition software.

![Figure 3: The Du Pont DSC Controlling Software Screen Shot](image)

The software used to control the DSC, record data, and analyze data is Thermal Analysis Software for Windows DSC 910 module. The controlling software shows the temperature of the furnace, sample, real time completion percentage of experiment, and experimental protocol. The experimental control protocol for this DSC; enter a description for each experiment, the sample weight, the start temperature, the end temperature, the heating rate, the holding time, and the sampling rate of data. The analysis software has the ability to perform analysis using data point labeling, DSC peak area, DSC fused peak area, Onset point calculation, Glass transitions, crystallinity, among other features.
A TA Q200 MDSC, this research grade DSC has modulated capabilities. This MDSC has three thermocouples, compared to two in the Du Pont model; one under the sample stage, the reference stage, and one in the middle of the cell between and below the reference and sample stage to better control temperature of the cell. This cell is also connected to a Refrigerated Cooling System 40 (RCS). The RCS allows for cooling during experiments, sub-ambient temperatures, and allows for a more accurate thermal analysis of samples. This RCS requires a purge gas to keep out moisture from the cell. Moisture inside the cell has the potential to damage the instrument and contaminate the accuracy of the experiment. The moisture can alter the rate at which the experiment is run. Also, while the cooler is in use if moisture is in the cell it may freeze and cause damage to the cell and cooler. In this study, Nitrogen is used as the purge gas. This MDSC has a more sophisticated control and analysis software.
The control software is the TA Instruments Advantage Software. This software allows for complete remote control of the DSC except for loading and unloading samples. The software has complete experimental setup control, showing live signal values, and a real-time plot of the data. The experimental setup allows the change between modulation and conventional DSC, different preset tests to be chosen, naming experiments, choosing sample pan type, sample size, comments section, where to save the data, ability to customize runs using a very easy to follow drag and drop format, control of the purge gas flow rate, among many others.
The TA Instruments analysis software is provided with the instrument. Once the file is open, there are too many analysis options to include. The ones that are included in this research include choosing an analysis section, integrating peak linearly, peak maximum, signal maximum, signal change, onset point, slope, annotation, choosing different signals to plot, and many more. Primarily, the analysis uses the heat flow (W/g) versus temperature to observe trends in the sample’s reaction. The reverse and non-reverse signals constitute modulated capabilities.
In order to properly characterize the reaction forming thin films, an optimum DSC experimental protocol needs to be established. Optimum conditions include sample size, heating rate, hermetic versus pinhole lids, and modulation versus conventional.

2.3.2 DSC Data Analysis

A Differential Scanning Calorimeter (DSC) measures the differences in energy provided to the sample as compared to that provided to the reference. The data can be reported in a variety of format; for instance, as shown in Figure 8, the DSC spectrum can represent the difference between the power (frequently referred to as “heat flow”) supplied to the sample as compared to that supplied to the reference, and it is typically reported per unit mass of sample. The heat flow data can be easily manipulated to yield important thermo physical properties such as, the specific heat of a sample and the change in enthalpy observed during phase changes or chemical transformations. Heat flow data from a typical DSC experiment is shown in figure 8.

Figure 8: Simplistic DSC Experiment
The region of the DSC spectrum highlighted in Figure 8 would correspond to a phase change or a chemical transformation. These regions are the focal point of the research reported in this thesis. To put these results in the proper perspective let us resort to the first law of thermodynamics to demonstrate how the manipulation of a typical DSC spectrum (data) can be used to extract information on specific heat and chemical reactions.

The manipulation begins by analyzing the first law of thermodynamics.

\[ dU = \delta Q - \delta W \]

The initial step is to identify the relationship between internal energy and enthalpy.

\[ \Delta U = \Delta H + \delta W_c \]

Using this relationship, the first law of thermodynamics expands to:

\[ dH = \left( \frac{\partial H}{\partial p} \right)_{T,x} dp + \left( \frac{\partial H}{\partial T} \right)_{p,x} dT + \left( \frac{\partial H}{\partial x} \right)_{T,p} dx \]

In order to simplify the first law of thermodynamics, the pressure change term is neglected, i.e.

\[ dH = \delta Q \]

Furthermore, if the relationship between \( C_p \) and heat flow:

\[ Q = \int mC_p dT \]
is differentiated as:

\[ dQ = mC_p dT \]

and assuming that the \( C_p \) is not a function of time.

\[ \frac{dQ}{dt} = mC_p \frac{dT}{dt} \]

Finally, inserting this into the first law of thermodynamics, the equation yields:

\[ \text{watts} = \left[ \frac{J}{\text{sec}} \right] = \frac{dH}{dt} = \frac{dQ}{dt} = mC_p \frac{dT}{dt} + f(t,T) \]

Where, \( \frac{dT}{dt} \) represents the heating rate used in the experiment, and \( f(t,T) \) quantify the thermal effects associated to a phase change, a chemical transformation, or both.

If we now focus our attention to the section highlighted in figure 8, where the thermal evolution is interpreted as associated to a phase or chemical transformation. In order to extract useful information from this DSC spectrum, the heat capacity and heat associated with the phase or chemical transformation must be isolated from each other.

Let us now interpret the data using the relationship derived from the first law of thermodynamics.

\[ \text{watts} = \left[ \frac{J}{\text{sec}} \right] = \frac{dH}{dt} = \frac{dQ}{dt} = mC_p \frac{dT}{dt} + f(t,T) \]

If we focus our attention to the region of the DSC corresponding to heating only (i.e., in the absence of any transformation), the equation becomes
\[
\frac{dQ}{dt} = mC_p \frac{dT}{dt}
\]

In other words, the heat capacity would correspond to the slope of the DSC spectrum affected by the heating rate, i.e.

\[
C_p = \frac{1}{m} \frac{dQ}{dt} \left( \frac{1}{\frac{dT}{dt}} \right) = \frac{1}{m} \frac{dQ}{dT}
\]

The section before the reaction needs to be used to extract the heat capacity by means of a simple application of least squares.

Once the heat capacity is known, the chemical or phase transformation can now be characterized by means of the relationship derived from the first law of thermodynamics. Notice that as the DSC spectrum corresponds to energy per unit mass, the original equation is then manipulated as:

\[
\text{watts} \frac{g}{sec \ast g} = \left[ \frac{J}{m \cdot dt} \right] = \frac{1}{m} \frac{dH}{dt} = \frac{1}{m} \frac{dQ}{dt} = C_p \frac{dT}{dt} + f(t,T)
\]

The heat capacity is now inserted into the first law of thermodynamics, and the resulting energy is correlated as the heat of reaction, i.e.,

\[
\frac{f(t,T)}{m} = \frac{1}{m} \frac{dQ}{dt} - C_p \frac{dT}{dt}
\]

This manipulation is the basis for extracting the heat of reaction and then continuing to perform kinetic analysis using the Borchardt and Daniels’ Method. This manipulation allows one to isolate the thermal evolution due to the transformation (the
total heat of reaction) and subsequent completion of the kinetic analysis through the Borchardt and Daniels’ Method (as explained in Chapter 4.1.3)

2.3.3 Phase Change Analysis

The thin film protective coatings in this study are generated by a process typically referred to as Chemical Vapor Deposition (CVD). CVD is the technique where a sample vaporizes and then deposits on a solid substrate to create the desired product. CVD is used in a variety of applications: insulation, creating protective coatings, synthesis of advanced materials, etc. CVD characterization requires the combination of chemical thermodynamics, kinetics, and transport phenomena. This study utilizes a CSU developed technique to create a protective coating on aluminum substrates using environmentally friendly precursors. This study explores the use of solutions of TBTPP and iron (II) acetate to form a protective coating on aluminum always via a CVD process.

Chemical Vapor Deposition requires the reaction to take place from vapor to thin film. The solution used in this study first initially in the liquid state, must be vaporized into the vapor phase. In order to vaporize the solution at the correct temperature for optimum CVD, experiments were performed to study the heating effects of the DSC heating rates of each solution. A phase change analysis has been performed involving different sample sizes and different heating rates observing the effects on the vaporization temperature. Three different heating rates and three different sample sizes were tested. The figure shows one example of the phase change analysis. The table combines all experiments into one table to shows the vaporization temperatures were shown to decrease as the sample size and heating rate decrease.
Figure 9: 20 °C/min Heating Ramp Boiling Point Analysis

Figure 9 is analyzed into two tables, one with a constant heating rate.

<table>
<thead>
<tr>
<th>Heating Rate (C/min)</th>
<th>Sample Mass (mg)</th>
<th>Lower Limit Temperature (C)</th>
<th>Upper Limit Temperature (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.51</td>
<td>282.2</td>
<td>295.1</td>
</tr>
<tr>
<td>10</td>
<td>0.97</td>
<td>278.3</td>
<td>289.6</td>
</tr>
<tr>
<td>10</td>
<td>0.62</td>
<td>266.3</td>
<td>278.9</td>
</tr>
</tbody>
</table>

Table I: Constant Heating Rate Phase Change Analysis

The other is constant sample mass.

<table>
<thead>
<tr>
<th>Heating Rate (C/min)</th>
<th>Sample Mass (mg)</th>
<th>Lower Limit Temperature (C)</th>
<th>Upper Limit Temperature (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.69</td>
<td>273.4</td>
<td>306.9</td>
</tr>
<tr>
<td>10</td>
<td>0.62</td>
<td>266.3</td>
<td>278.9</td>
</tr>
<tr>
<td>2.5</td>
<td>0.63</td>
<td>238.5</td>
<td>252.2</td>
</tr>
</tbody>
</table>

Table II: Constant Sample Mass Phase Change Analysis
These two tables represent the results from the phase change analysis. The result from this analysis is that by increasing the sample mass and/or the heating rate, the vaporization temperature will also increase.

2.3.4 Sample Enclosure Analysis (Hermetic versus Pinhole)

The three choices of DSC samplers consist of open pans, hermetic pans, and pans sealed with pinhole lids. These three choices will provide different results. The open pan was used in the boiling point analysis. Experiments conducted in the open pans readily show phase changes. Shown in figure 9, one can clearly see the vaporization point of the sample. In figure 10, on the other hand, it is difficult to see the change of state using a pinhole or hermetic container.

Figure 10: Hermetic pan using a 20 °C/min heating rate versus sample size

Figure 10 shows the spectrum for traditional DSC data using a 20 °C/min heating rate in hermetically sealed samples. Samples analyzed in hermetically sealed pans represent a non-isothermal constant volume batch reactor experiments. The one downfall with the hermetically sealed pans is the pressure building up. Vaporizing the liquid sample creates
a significant increase in pressure. This pressure buildup can break the hermetic seal which yields a failed experiment.

Figure 11: Pinhole at 20 °C min versus sample size

Figure 11 shows the DSC spectrum obtained from a sample in a sealed pan with a pinhole lid. The idea of a pinhole lid is to allow pressure equilibrium with the surroundings eliminating any pressure build up. In other words, the pinhole allows for the vaporization of the sample without changing the pressure of the system. This constant pressure allows for the semi-batch non-isothermal design equations to be used in the analysis of the data.
Figure 12: Experiments in pans with Pinhole lids versus Hermetic Sealed

Figure 12 provides a comparison between hermetically sealed pans and those with pinhole lids. A rupture possibly can be seen towards the end of the experiment in the hermetically sealed pan. The pinhole shows the vaporization as well as the hermetically sealed pans, but the pinhole continues to show a possible reaction around 350 °C. The hermetically sealed pan possibly shows a slight reaction at 350°C as well, but typically is not considered because of the pressure build up.

2.3.5 Effect of Heating Rate

The heating rate is the most important parameter to be characterized when formulating a protocol. The heating rate dictates length of the experiment, the time spent vaporized, the time it takes to vaporize the sample. The vaporized solution has been shown to be very susceptible to the temperature. The temperature profile determines whether or not a chemical reaction will be detected through the DSC. The protocol to identify the optimum heating rate consists of experiments using heating rates from 20 °C/min to 1 °C/min. The best results were found using a heating rate for the range of the reaction (shown in Fig. 16 from 300°C and 400°C) of 2.5 °C/min.
Figure 13: Heating Rate of $20 \ \degree C/min$ and sample sizes

Shown in figure 13, the heating rate does not show anything. It briefly shows the vaporization around 300$\degree$C but shows no reaction. The heating rate shown above is too quick to observe the reaction.

Figure 14: Heating Rate of $10 \ \degree C/min$ and sample sizes

The above and below figure show the heating rates also being too quick to observe the reactions. The sample sizes contain different amounts of iron (II) acetate and will affect the amount of heat required to heat each sample. Therefore, the slopes will
remain the same between experiments, but the amount of heat flow will change because the solution is shown to be close to homogeneity but not.

Figure 15: Heating Rate of 5 °C/min and sample sizes

Figure 16: Heating Rate of 2.5 °C/min and sample sizes
Figure 16 reveals the reaction taking place. This shows an increase in heat to complete the reaction and then a decrease after the reaction is completed. At $2.5 \frac{^\circ C}{\text{min}}$ the reaction shows to be able to be detected at approximately 1 $\mu L$.

### 2.3.6 Effect of Sample size

The material and energy balance surrounding this semi-batch system are strong functions of the amount of sample and the temperature profile. If too little sample is used, the sample will vaporize and quickly leave the system before reacting. If too much sample is used, the sample will vaporize either occupying the full volume of the container unable to react with the aluminum substrate, or potentially rupture the hermetic seal and quickly leave the system. Through experimental choices, the system has been tested for 0.5 $\mu L$, 1 $\mu L$, and 1.5 $\mu L$ samples of solution. From extensive experiments, it has been shown that the 1 $\mu L$ shows the most reactivity. A volumetric pipette was used to ensure relatable sample sizes in the comparative experiments. Shown in figure 16 will reveal the reaction.

### 2.3.7 Isothermal DSC Data Analysis

The results for the experimental heating rate provide a lingering question. Why is the reaction detected very clearly during some experiments but absent during others? The residence time of the sample in the vapor state may need to be increased to favor the reaction with the aluminum. Certain experiments spent very little time between the reaction temperatures at higher heating rates, but this fails to explain why the reaction is not shown during much slower heating rates. Another issue may be the lack of homogeneity of the solution. Some samples may have varying amounts of iron (II) acetate and this leads to coatings being deposited at different temperatures. In order to
find the answer to these questions, an idea of prolonging the amount of time the reactant is in the vapor phase was implemented by programming an isothermal stage at 300°C and then continuing the heating rate of $2.5 \frac{^\circ C}{min}$.

Isothermal stages have been applied to the experimental protocol to observe their effects.

Figure 17: Isothermal 5 minutes at 300°C

Figure 17, shows no variations from other heating rates. There is fluctuation at 390°C. This fluctuation can be due to a lingering reaction or presence of films forming while reactants still in the vapor phase yielding noisy DSC data.
Figure 18 reveals the pros and cons of using isothermal stages. The data of the 0.5 µL sample provides noisy results that point to a film being formed while vapors still existing in the sample. The 2 µL sample does not yield any type of reaction being shown. The important analysis from this figure is the 1 µL sample. It yields zero heat flowing into the sample. This is because all of the reactants have through the pinhole leaving nothing to heat. This shows that the isothermal stage must be precisely at the vaporization point or the risk of losing excess reactants is high. The 0.5 µL was adjusted and held isothermal at its vaporization point and the results shown above show reactants still in the pan reacting.

The idea of this analysis is to vaporize the solution during an isothermal stage and then perform the heating ramp to observe the reaction. The reactants starting in the vapor phase allows the reaction to be detected versus temperature.
Figure 19: Isothermal 20 minutes 0.566 mg

Figure 19 shows the vaporization occurring during the isothermal period of the experiment.

Figure 20: Isothermal 20 minutes

Figure 20 shows an increased amount of variation. The smallest sample changes phase at 390°C. This change of state can be vapor to film or some other thermal effect.

The protocol to observe a reaction using an isothermal stage is to properly adjust the isothermal temperature to accommodate the sample size. The temperature needs to be
precisely before the vaporization to allow for the vaporization during the isothermal period. The heating rate after the isothermal will continue to be characterized to identify the reproducible reaction, but this research suggests $2.5 \, ^\circ C / \min$.

2.3.8 Experimental Protocol

From the previous experiments it has been shown to produce results using a 1 µL sample and begin the experiment at 200°C performing a heating rate of $2.5 \, ^\circ C / \min$ to 400°C. Kinetic Analysis will be performed using the runs that created DSC detectable reactions through this experimental protocol. Future analysis may reveal a more reproducible experimental protocol, but current research uses this one.

2.3.9 Modulation versus Conventional DSC

The instrumentation provides the choices for this research as Modulated DSC and tradition DSC. This study intends to study both the advantages and disadvantages of modulation compared to conventional DSC in the analysis of thin film deposition. Reproducibility and characterization of the chemical vapor deposition reaction kinetics is an important goal of this research. In order to consistently reproduce the CVD reaction, the transition between vaporization and the formation of the protective coating needs to be characterized. Modulation and conventional DSC are explored to provide an in-depth analysis to these phenomena.

Conventional DSC study the response of a sample to linearly varying or isothermal temperature profiles. DSC enables the characterization of the sample material properties such as transition temperatures, melting and crystallization, and heat capacity. Modulated DSC can increase the amount of information that can be obtained from a single DSC
experiment. Some modulated capabilities include: Measurement of heat capacity and heat flow in a single experiment; separation of complex transitions into more easily interpreted components; increased sensitivity for detection of weak transitions; increased resolution of transitions without loss of sensitivity; increased accuracy in the measurement of polymer crystallinity; and direct determination of thermal conductivity (TA Instruments). For instance, results from a conventional DSC are shown in Figure 21.

![Figure 21: Conventional DSC results](image)

Modulation allows for a more complex heating profile than simply a linear heating. Modulation combines two conventional DSC experiments into one: a traditional linear (average) heating rate, and a sinusoidal (instantaneous) heating rate (TA Instruments). This allows a more exact analysis to be performed on the chemical reaction. This approach suggests that when the chemical reaction occurs, simply target the temperature range with a modulated analysis to increase sensitivity in the heat flow analysis.

Modulation creates a temperature profile that increases the average temperature linearly using sinusoidal amplitudes to study the response to fluctuations. For example, instead of creating a temperature profile starting from 200°C and ending at 300°C
increasing at $3 \, ^\circ C / \text{min}$, modulation provides a similar starting temperature of 200$^\circ$C and ending at 300$^\circ$C with a $3 \, ^\circ C$ increase but a +/- of 0.5$^\circ$C per 40 second period. This allows for an in-depth analysis of the sample and provides a precise temperature point where changes may occur in the sample. This data can be shown through a regular heat flow graph similar to the conventional DSC or showing a modulated heat flow. Modulated heat flow is the exact response to the sinusoidal, and the conventional DSC heat flow would be the average of the modulated heat flow. An example of modulated heat flow DSC results is shown below:

![Figure 22: Showing Modulated heat flow](image)

A preset modulated experiment in the MDSC is the ability of “heat only”. This provides a sinusoidal temperature profile onto the experiment without cooling the experiment at any time. The computer automatically adjusts the amplitude so that it will never cool the experiment. This is useful to observe heating effects to the sample without cooling. This is convenient if the reaction being detected is not reversible. If the reaction is reversible, cooling will be more precise of the temperature profile concerning the reaction,
but if the reaction is irreversible the cooling with affect the results. An example of this modulated heat only DSC result is shown:

![Figure 23: Showing Modulated Heat Only Graph](image)

2.3.10 Reference Pan Analysis: Empty or Pure Durad?

The DSC measures heat flow into the sample compared to a reference pan’s heat flow. By adding a sample into the reference pan will be a difference of heat flow between the two samples. Pure ester phosphate is the base lubricant used in the solutions. Ester phosphate requires iron to be present to create a coating. Using aluminum pans, no iron will be present.

Ideally, the filled sample of ester phosphate of equal size to the sample size will allow for a better understanding of the reaction taking place. This experimental setup will allow a better understanding of the iron (II) acetate additive’s effect on the solution. The only effects the DSC should record would be the effects caused by the additive. Both samples will have an observed phase change, but only one pan should produce a reaction due to the iron additive.
Performing this analysis the sample and reference pan were composed of the same volume and approximate weight. The experimental protocol heated from 40°C to the Boiling Point (found from the phase change analysis), then subjected to a 20 minute period of isothermal temperature to observe phase change, and then heated at $2.5 \frac{^\circ C}{\text{min}}$ to 400°C.

Initial results provided noisy data of the highest volume of sample. Shown below in figure 24, this noise could be due to difference in sample size, possibility of liquid lingering in solution compared to all vapor in other pan, among others. This noise seems to be reoccurring and needs to be addressed in future studies.

![Figure 24: Equivalent Sample Size of TBTPP filled in reference Pan](image)

Shown above in figure 24, as volume decreased the data became less noisy. At the lowest volume it is showing a clear thermal effect at 388°C. This effect can be a late reaction or a complete phase change from vapor to a film. This lowest volume was attempted to be repeated experimentally. Shown below in figure 25, the results seem to
be inconsistent and need future analysis. There seems to be a continuing effect near 388°C that needs to be addressed in the future.

Figure 25: Filled reference Pan and Sample of 0.5 µL

2.4 Type F21100 Tube Furnace

The laboratory Thermolyne Type F21100 Tube Furnace with a mullite tube is used for decomposition experiments. The furnace schematic, (shown in Figure 26), a thermocouple provides a record of the temperature of the stage calibration between the stage and furnace must be first performed in order to provide a correct assessment of the heating rate. The furnace chamber is heated by heating elements embedded in a refractory material. The tubular chamber is insulated with ceramic fiber insulation. The furnace chamber is supported by the control base which also houses the electrical connections. Two types of controls are used Manual, and Single set point control. This research uses the single set point control. An electronic control enables the user to bring the furnace up to a preset temperature and hold the temperature.
The solution is poured into the cylindrical hole next to the coupon, after which the stage is pushed into the appropriate location within the mullite tube. Once the stage is in the appropriate position inside the tube, the furnace is programmed to run a predesigned temperature profile. The furnace has limited temperature controls. The furnace has the ability to obtain a constant heating rate and become isothermal. These experiments desire a uniform coating to be created, and consistent heating rates are used to produce uniform coatings.

The heating rate used in the furnace is derived from the DSC heating rate experiments. The DSC heating rate analysis was used to find the ideal heating rate to analyze the deposition reaction in the DSC. This heating rate is now used in the scaled up experiment, the furnace. This heating rate provides the optimum heating rate to produce the deposition reaction and is now continued to be used to create the deposited coatings.
CHAPTER III

FORMULATION OF MATHEMATICAL MODEL

3.1 FORMULATION OF A MATHEMATICAL MODEL

Preliminary research on protective coatings on ferrous substrates (Nagarajan et al., 2006) employed a modified thermal gravimetric analyzer (TGA) to study the deposition of thin films for wear and friction control on iron-based alloys. In this research, Nagarajan formulated a phenomenological model for coating a metallic substrate using ester phosphates as precursors.

This model uses a pseudo-steady state approximation to analyze a combined transport phenomena and chemical reaction problem. The coating mechanisms can be better understood as represented in the schematic of Figure 27.
Figure 27: Schematic of the film deposition process adapted from (Nagarajan et al., 2006)

In this schematic, three clearly distinguishable phenomena can be identified.

(1) The gas transport flux representing the vaporized ester phosphate transports from the sample pan to the interface between film and gas.

\[ F_1 = k_m (C_G - C_S) \]

(2) The ester phosphate diffuses through the growing film to the reaction surface.

\[ F_2 = -D \frac{(C_0 - C_L)}{L} \]

(3) As the ester phosphate reaches the surface of the substrate, the CVD reaction takes place. Assuming that the surface reaction can be characterized by an overall reaction of the power-law type, this flux can be written as:

\[ F_3 = \frac{K_f C_f^n}{S_y} \]

An observation is that in a film deposition process diffusion is occurring through a growing film. An assumption drawn is that the thickness of the film is moving at a much slower rate than mass diffusion occurs. Therefore, a key assumption made in this model was that the isothermal film growth process can be approximated as a pseudo-steady state.

The present work differentiates itself from the previous work in several ways. One of the fundamental differences is the use of the DSC instead of the TGA, i.e. a non-isothermal process. Another key difference is that while films grown on iron-based
substrates have a thickness ranging between 100-300 nm; in the current research much thinner (<50nm) protective coatings are deposited on non-iron substrates.

Let us now examine some of the similarities. Figure 28 depicts representative data from Nagarajan’s research (Nagarajan et al., 2006), where the isothermal deposition period can be clearly distinguished (as indicated in the figure 28).

Figure 28: TGA Experimental Data adapted from (Nagarajan et al., 2006)

Figure 28 provides the experimental data of the weight of the deposit versus the temperature and time on coatings from initial heating through the isothermal region.

The data can be linearized as:

\[
\frac{t - t_0}{W - W_0} = \frac{\tau_R}{W^*} + \frac{\tau_D}{(W^*)^2} (W + W_0)
\]
By linearizing the data one can identify the control mechanism in example, either kinetically controlled or a combined diffusion and kinetic control rate shown in Figure 29.

Clearly Shown in Figure 29 is the kinetically-controlled region and the region that combines kinetic and diffusion mechanisms. One can see that the kinetically controlled region is where thin films are deposited.

In the kinetically controlled region, the characteristic time of the reaction is significantly larger than that of the diffusion. This suggests diffusion occurs at a much faster rate than that of the surface reaction.

The reaction is assumed to consume all reactants that reach the surface by diffusion. This assumption allows the accumulation term to be neglected and the model can now be solved as a diffusion problem through a slowly growing film.
The current research focuses on films that are thinner than those investigated in previous research. These thinner films fall into the kinetically controlled region mechanism. This mechanism then needs to be characterized by the surface reaction kinetics and a material balance on the surface.

The surface reaction is again assumed to follow a power-law type kinetics, i.e.

\[ r_s = -k_i C_i^n \]

Where \( C_i \) is the concentration of ester phosphate at the reaction interface.

Following a similar formulation to that proposed by Nagarajan, the mass balance in the film becomes:

\[
\frac{\partial}{\partial x} \left[ D \frac{\partial C}{\partial x} \right] = 0
\]

Subject to the following boundary conditions:

\[
k_m (C_G - C_s) = -D \frac{\partial C}{\partial x} \quad \text{at } x = 0
\]

\[-D \frac{\partial C}{\partial x} = k_i \frac{C_i}{S_a} \quad \text{at } x = L \]

Where,
Table III: Variables of Mathematical Model

Nagarajan showed that the solution to this problem is:

\[ C(x) = C_o - \left( \frac{k_r}{DS_n} C_t^n \right) x \]

Current research utilizes a DSC to measure heat flow versus temperature and time in non-isothermal experiments. Steady state will not be achieved in these circumstances. Nagarajan utilized TGA to perform isothermal deposition experiments. She assumed a reaction order to analyze the data and required multiple experiments to extract the temperature-dependent parameters.

A key difference between current research and previous research is the ability to measure non-isothermal heat flow data. This experimental data can be shown to follow the constant volume non-isothermal batch reactor model. Indeed, the design equations can be manipulated as follows:

\[ -\frac{dC_A}{dt} = r_A \quad (1) \]
With, \( r_A = -kC_A^n \)

And \( k_{(T)} = k_{(T^0)} \exp \left[ \frac{-E}{R} \left( \frac{1}{T} - \frac{1}{T^0} \right) \right] \)

\( C_A = C_A^0 (1 - x_A) \)

Therefore, Equation (1) can be linearized as:

\[
\ln \left( \frac{dx_A}{dt} \right) = Z - \left( \frac{E}{R} \right) \left( \frac{1}{T} - \frac{1}{T^0} \right) + n \ln (1 - x_A)
\]

\( Z = k_{(T^0)} \left( C_A^0 \right)^{n-1} \)

With, \( Z = k_{(T^0)} \left( C_A^0 \right)^{n-1} \)

This manipulation allows the concentration versus temperature to be manipulated into conversion versus temperature. This allows the current analysis to extract all the parameters, namely the activation energy, reaction order, and reaction rate constant from a single experiment. Previous research required several experiments to extract this data because of the isothermal experiments were used in addition to refine the assumption of the reaction order. Current research allows the parameters to be extracted using a significant amount of fewer experiments.
4.1 Kinetic Analysis

The Differential Scanning Calorimeter (DSC) records experimental data of heat flow and temperature versus time. To simplify the analysis of this data, certain assumptions can be made regarding the reacting environment. The reaction creating the protective coating through chemical vapor deposition is studied in a closed pan with a pinhole lid. Shown in Figure 30, the reacting environment of a semi-batch reactor contains the sample being studied.
Therefore, assuming a semi-batch reactor with a negligible outflow of reactants, the constant volume, non-isothermal batch reactor design equations are applied enabling the differential method of kinetic analysis to be used.

There are two methods of extracting reaction kinetic parameters from this type of experimental data: (i) the differential method of kinetic analysis and (ii) the integral method of kinetic analysis. The integral method requires an integration of the model. This poses a problem because the experiment is non-isothermal and the reaction order is unknown.

4.1.1 Integral Method of Analysis Example

For a general reaction with kinetics of the power law type, the mole balance for a constant batch reactor is:

\[-\frac{dC_A}{dt} = kC_A^n\]

where $C_A$ is the concentration of species A; $k$ is the reaction rate; and $t$ denotes time; with the limit $C_A = C_{A0}$ at $t = 0$ this equation can be easily integrated to yield

For instance, for $n=1$ and Isothermal Conditions:

\[\ln \frac{C_{A0}}{C_A} = kt\]

This analysis is then used to graphically extract parameters by plotting $\ln \frac{C_{A0}}{C_A}$ vs. $t$. This graph provides the slope of $k$ (reaction rate).
Due to the unknown reaction order of this research and the dependency of reaction rate on temperature, and the dependency of the temperature on time, the differential method of analysis will be exclusively used.

4.1.2 Differential Method of Analysis

The following example uses experimental data acquired with a TA Q200 MDSC data. The primary parameters are the reaction order (n), activation energy (E), and the reference rate constant (k₀). Using the differential method of analysis for batch reactors data the sequence of equations initiating from the design equations for constant volume batch reactors assuming power law kinetics:

\[
\frac{dC_s}{dt} = r_s - \frac{Q^0}{V} C_G
\]

C_s is the surface concentration of the reacting film; C_G is the concentration in the gas phase of TBTPP reacted. C_G=f(C_s)

\[
r_s = -kC_s^n
\]

\[
k_{(T)} = k_{(T^0)} \exp\left[\left(\frac{-E}{R}\right)\left(\frac{1}{T} - \frac{1}{T^0}\right)\right]
\]

For simplicity, the concentration at the surface (C_s) is from now on going to be referred to as C_A. Also, the design equation is shown as a semi-batch, but for analysis it will be shown that the amount of reactants leaving through the pinhole is discussed later in the kinetic analysis, and for the purpose of illustration assumed a batch reactor.

\[
C_A = C_A^0(1 - x_A)
\]
This allows for the important parameters, such as activation energy \(E\) and reaction order \(n\), to be statistically analyzed.

\[
\ln\left(\frac{dx_A}{dt}\right) = \ln Z = \left(\frac{E}{R}\right)\left[\frac{1}{T} - \frac{1}{T^0}\right] + n \ln(1 - x_A)
\]

\[Z = k_{(T^0)}(C_A^0)^{n-1}\]

### 4.1.3 Illustrative Example using Borchardt and Daniels Method

If the data recorded is plotted as heat flux versus temperature one can clearly see the occurrence of a chemical reaction as shown by the endothermic peak in the proximity of 350°C. The raw data (Figure 31) suggests that the reaction occurs approximately between 325°C and 375°C.

![Figure 31: Q200 Experimental Data of DSC Experiment](image)

A common baseline is now drawn through the reaction data using the data where there was no reaction occurring.
Figure 32: Q200 Experimental Data + Baseline

The Du Pont DSC provides data that contains a significant amount of noise. Noise is filtered using an average neighboring and smoothes the data based on a sensitivity analysis (see Appendix B).

Appendix B, the filtering technique produces data showing a significant decrease in noise compared to the raw data. Filtering is crucial for an accurate analysis, if data is required via the Du Pont DSC. The presence of noise is the reason why kinetic analysis is performed using experimental data from the TA Q200 MDSC. Current experimental data of the MDSC contains approximately 18,000 data points. The lack of noise in the MDSC experimental data allows a filter to be used to reduce the amount of data points to a smaller amount by taking averages and not losing accuracy of the experimental data. The accuracy is continued because the average of the noise free data is experimental data.

The filtered data is now truncated between the reaction initial and final temperatures along the baseline data. This baseline will create a value for the data to be related to. This normalization is a change of axis, from a diagonal axis to a zeroed x-axis. The reaction data is subtracted by the baseline data to normalize the data.
Figure 33: Chemical Reaction Analysis Section Data + Baseline

The data is normalized following the Borchardt and Daniels’ method (Borchardt et al., 1956), which uses the general rate equation to describe the dependence of the rate of reaction on the amount of material present. The conversion of the reaction is assumed to correspond to the partial heat of reaction divided by the total heat of reaction. Because the energy creating the phase change from liquid to vapor is prior to the deposition reaction approximately 260 °C (Figure 31), the heat of reaction can be estimated by integrating the experimental data using the trapezoidal rule.
Figure 34: Curve symbolizes normalized heat flow of exothermic raw data

Figure 34 represents the experimental data observed; figure 35 (below) shows the result of the Borchardt and Daniels’ method.

Figure 35: Conversion Figure of Time and Temperature

Figure 35 shows the conversion of the reaction from the experimental data plotted against temperature and time. This graph is the result of the Borchardt and Daniels Method. The Conversion data plotted above is crucial to extracting the reaction kinetic parameters.
4.1.4 Extraction of Kinetic Parameters

\[
\ln\left(\frac{dx_A}{dt}\right) = \ln Z - \left(\frac{E}{R}\right)\left[\frac{1}{T} - \frac{1}{T^0}\right] + n \ln(1 - x_A)
\]

\[
Z = k_{(T^0)}(C_A^0)^{n-1}
\]

In order to solve the above equation for \(Z\), \(\frac{E}{R}\), and \(n\) a multiple linear regression model will be used to fit the data. The model described above has the following generalized form:

\[
y = a_0 + a_1x_1 + a_2x_2 + \ldots + a_kx_k + E
\]

Extracting these parameters consist of using a least squares technique.

\(Z\) is not a kinetic parameter, but a grouping of constants including the initial concentration \(C_A^0\). The initial conditions of the reaction consist of the reaction temperature and no deposits made. Corresponding to the figure 27, at initial conditions:

\[
C_G = C_A^0
\]

This is a safe assumption because of the lacking of a film to diffuse through.

Assuming an ideal gas, Raoult’s law, and \(P=P_{Sat}\) at the boiling point, (yielding an atmospheric system pressure), it is shown that the liquid mole fraction will equal the vapor mole fraction. For this instance, the liquid is assumed pure solution. This is a broad assumption, but an order of magnitude analysis was performed to observe the error between a pure assumption and a very small vapor fraction. The results are shown in Appendix F, yielding the insignificant effect on the reaction rate constant.
Using ideal gas assumption,

\[ C_G = C_A^0 = \gamma \frac{P_o}{RT_o} \]

Where, \( P_o \) is the pressure of the system (atmospheric), \( R \) is the universal gas constant, \( T_o \) is the initial reaction temperature. The \( C_A^0 \) will vary between experiments due to the initial reaction temperature.

Further manipulation will yield the reaction rate constant of the reaction (\( k_{T_o} \)).

\[ Z = k_{(T_o)} (C_A^0)^{n-1} \]

\[ \ln Z = \ln k^o + (n-1) \ln C_A^0 \]

The least squares extraction technique extracts

\[ Y_o = \ln Z \]

Extracting \( k_o \) manipulates the equation to

\[ k_o = \frac{e^{Y_o}}{C_A^{(n-1)}} \]

The corresponding errors to \( k_o \) are derived as

\[ E_{k_o} = \left| \frac{\partial k_o}{\partial Y_o} \right| \cdot E_{Y_o} + \left| \frac{\partial k_o}{\partial n} \right| \cdot E_n + \left| \frac{\partial k_o}{\partial C_A} \right| \cdot E_{C_A} \]

\( E_i \) is the error included in the corresponding variable (\( i=Y_o, n, \) and \( C_A^0 \)).
\[
\frac{\partial k_n}{\partial Y_n} = \frac{e^{Y_n}}{C_A^{\alpha (n-1)}}
\]

\[
\frac{\partial k_n}{\partial n} = \left[ -e^{Y_n} * C_A^{\alpha (1-n)} \ln C_A \right]
\]

\[
\frac{\partial k_n}{\partial C_A} = \frac{e^{Y_n}}{C_A^{\alpha (n-1)}} (1-n)
\]

The reaction rate constant and the error associated with it can now be extracted with the respect to the other extracted parameters.

But before the parameters are extracted, the data points that do not conform to the batch reactor assumption need to be identified and removed.

4.1.5 Linearization of Data

Linearization of the data using the results of the differential method of kinetic analysis provides a means to assess what part of the data does not conform to the batch reactor assumption.

A graph of \( \ln \frac{dx_A}{dt} \) versus \( \frac{1}{T} - \frac{1}{T^*} \) is required. The true accuracy of the results is shown if the data conforms to a linear trend.
Figure 36: Linearized Data used for Graphical Analysis

Figure 36 provides linearized data. The graph shows that the data deviates from the linear model at the beginning of and at the end of the reaction. In order to use

$$\ln \left( \frac{dx_A}{dt} \right) = \ln Z - \left( \frac{E}{R} \right) \left[ \frac{1}{T} - \frac{1}{T_0} \right] + n \ln(1 - x_A)$$

to extract the reaction kinetic parameters, the data that conforms to the batch reactor assumption needs to be used and the data that does not conform needs to be neglected. If all of the data was used, error would show in the parameters because of the actual semi-batch system. The linear regression shown in the graph has a great deal of error in it currently, but once the data is reduced to include the batch reactor assumption the linear regression becomes more accurate.
Figure 37: Linearized Data used for Graphical Analysis Truncated for Batch Reactor Assumption

Figure 37 reveals the first data selection of a batch reactor assumption. This technique uses the data to create a linear regression that has the least error involved in the data. This filtering technique can be applied repeatedly until further filtering does not affect the estimated parameters significantly. A data analysis that includes a statistic (e.g. the student’s t) is therefore required.

The corresponding values of the parameters along with their standard errors are shown in Table III. The program that performs this sequential linearization process and completes the kinetic analysis is included in Appendix A.
4.2. Kinetic Analysis Results

The Kinetic Analysis results from the extracted experimental data are provided in both graphical and table formats. The parameters that are being plotted in Figure 38 are the initial linearized experimental data versus the filtered linearized experimental data. No-Filter refers to the initial data, and the filtered refers to the filtered linearized data. The first parameter shown is the reaction order.

![Reaction Order Parameter Plot](image)

Figure 38: Reaction Order Parameter Plot

Figure 38, the reaction order reveals approximately a single order reaction. Additional experiments will be able to provide a more accurate reaction order for future analysis.

Activation Energy is the next parameter that was extracted and plotted.
The activation energy varied more than anticipated. Multiple experiments need to identify a more accurate result. From Table III, the activation energy (E) [kJ/mol] would be taken approximately as 300 kJ/mol.

The following tables represent the individual values plus the corresponding errors involved in the kinetic analysis.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>n</th>
<th>(±)</th>
<th>E  (kJ/mol)</th>
<th>(±)</th>
<th>ko m^3/mol</th>
<th>(±)</th>
<th>To [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.7</td>
<td>0.03</td>
<td>200</td>
<td>8</td>
<td>10</td>
<td>2</td>
<td>331.25</td>
</tr>
<tr>
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<td>1</td>
<td>0.03</td>
<td>600</td>
<td>20</td>
<td>8</td>
<td>1</td>
<td>343.7</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>0.03</td>
<td>300</td>
<td>10</td>
<td>5</td>
<td>1</td>
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<tr>
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<td>0.05</td>
<td>300</td>
<td>30</td>
<td>20</td>
<td>4</td>
<td>360.85</td>
</tr>
</tbody>
</table>

Table IV: The Kinetic Analysis Results of Linearized Data

Table IV shows the initial parameters extracted from the linearized data and the corresponding errors involved in each parameter.
Corrected Estimates (after first correction)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>n</th>
<th>(+/-)</th>
<th>E (kJ/mol)</th>
<th>(+/-)</th>
<th>ko m^3/mol</th>
<th>(+/-)</th>
<th>To [C]</th>
</tr>
</thead>
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</tr>
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<td>10</td>
<td>8</td>
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<tr>
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<td>200</td>
<td>20</td>
<td>20</td>
<td>3</td>
<td>360.85</td>
</tr>
</tbody>
</table>

Table V: The Kinetic Analysis Results of Single Pass Filtered Linearized Data

Table V shows the parameters extracted from a filtered linearized data and the corresponding errors involved in each parameter.

As it was mention above, if the filtering technique is then applied until further filtering does not affect the estimated parameters significantly we can obtain the optimum values of the kinetic parameters. For experimental set “C” for instance, the final parameters would be:

<table>
<thead>
<tr>
<th>Optimum Filtered Estimates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters</td>
</tr>
<tr>
<td>------------</td>
</tr>
<tr>
<td>C</td>
</tr>
</tbody>
</table>

Table VI: The Kinetic Analysis Results of Optimum Filtered Linearized Data

A more elaborated data analysis based on statistical principles to formulate a convergence criterion is under development.

4.3. Kinetic Analysis Discussion

A protocol to analyze deposition reaction kinetics using a conventional DSC was formulated in this research. The technique using the method of least squares provides the reaction kinetic parameters and their corresponding errors associated with each experiment.
Shown in the results (Sec. 4.2), each result exhibits and error less than 10%, but the majority of results exhibits an error less than 6%. This error represents an accurate protocol to extract the reaction kinetic parameters.

One key aspect to this protocol is to identify the reaction taking place in each experiment. A simple misidentification using this current protocol will provide erroneous results. The current protocol asks the user to identify the temperature range of the reaction, in order to truncate the data and extract conversion data. This range then creates a linear baseline from the temperature range. By choosing a temperature range that is either too early or too late from the reaction will create a linear baseline that does not correctly identify a non-reacting linear profile. The temperatures of the reaction range need to be identified in this protocol and a line created. Future studies should develop a protocol that does not require the user to enter the reaction temperature range.

The results shown in Section 4.2 provide initial numbers to compare to future studies to identify comparable results.
CHAPTER V

NUMERICAL SIMULATION

5.1 Introduction

One of the goals of this research was to integrate the kinetic analysis with numerical modeling to investigate the process scale up. The kinetic analysis section describes the procedure of formulating the deposition model and extracting/estimating the kinetic parameters.

The purpose of this simulation is to reproduce the physical environment of a deposition furnace and to predict thermodynamics, transport phenomena and fluid dynamics, and reaction kinetics of an in-silico deposition experiment which would mimic the experiments in the furnace.

COMSOL is a finite element modeling interface that allows the user to readily set up and solve space and time dependent multiphysics problems. The module that is used in this research is the Chemical Engineering Module.

5.2 Model Definition

This research examines the current model as a deposition furnace compressed of a mullite tube inside a radiation furnace. The schematic of the furnace set up is shown in figure 26 and figure 40.
Figure 40: Thermolyne F21100 Tube Furnace Schematic Diagram (Reye et al., 2004)

The solution used as a precursor is placed in a well on the deposition stage. This stage has the aluminum stamp to be coated attached to the top. The stage is placed inside of the mullite tube. The mullite tube is then heated with a desired heating dynamics that would ensure coatings that are produced on the aluminum stamp. During the deposition, the furnace is inside a fume hood, which could create a slight flow of air through the mullite tube.

The full 3D representation of the mullite tube and the solution stage is shown in figure 41.
In an initial approach, if angular symmetry is assumed and end effects are neglected, this 3D model can simplify into a 2D model. Further studies will expand this model into a fully 3D simulation.

Figure 41: (a) 3D Geometry of Mullite Tube and Solution Stage (b) x-y 2D side representation of Geometry (c) y-z 2D side representation of Geometry

Figure 42: Modeling the geometry in 2D
5.3 Chemistry

As stated in Chapter 3: Formulation of a Mathematical Model, a power law kinetic model is used \( r_s = -kC^n \). This assumption models the deposition mechanism assuming no intermediates are formed during the deposition. Using this simple assumption, the deposition reaction would be:

\[
mA \rightarrow^k F
\]

Where A is the precursor, F is the film created resulting from the CVD mechanism, \( m \) is the stoichometric coefficient, and \( k \) is the reaction rate, shown to be manipulated to contain activation energy, and a reaction rate constant at a specific temperature as in Chapter 3.

The conversion of species A in the furnace is a function of the residence time, and because transport mechanisms affected by fluid flow. As the deposition is highly influenced by the temperature distribution, a coupled system of transport equations will describe the phenomena occurring in the furnace.

5.4 Momentum Transport

This model initially assumes the flow through the mullite tube is laminar and can be described by the incompressible Navier-Stokes equations:

\[
\rho \frac{\partial \vec{u}}{\partial t} = -\nabla \cdot \eta \left( \nabla \vec{u} + \left( \nabla \vec{u} \right)^T \right) + \rho \vec{u} \cdot \nabla \vec{u} + \nabla p = \vec{F}
\]

\[
\nabla \cdot \vec{u} = 0
\]

Where, \( \eta \) denotes the dynamic viscosity (Ns/m\(^2\)), \( \vec{u} \) the velocity (m/s), \( \rho \) the density of the fluid (kg/m\(^3\)), \( p \) the pressure (Pa), and \( \vec{F} \) is a body force term (N/m\(^3\)).
The equation describes the flow of incompressible Newtonian fluids. As an initial modeling assumption, the fluid (air), is modeled as a low velocity developed flow through the mullite tube, and is modeled as Newtonian and incompressible. Future models will represent the flow using more accurate models. The initial model in this simulation provides a basic flow through the mullite tube, changing the type of flow will be studied as a possible deposition modeling tool in future models.

Additionally to the domain equations, boundary conditions need to be specified. At the inlet a velocity normal to the boundary is specified:

\[ \mathbf{u} \cdot \mathbf{n} = u_o \]

This specific velocity is found from a simulation of a mullite tube inside of a fume hood. The model of the mullite tube in the laboratory fume hood can provide an estimate for the velocity of air at the inlet. This velocity that is found at the inlet is assumed initially to be a flat profile, but quickly develops through the mullite tube.

Let us examine the results from a fume hood model.
Figure 43: Velocity Field of Fume Hood Simulation

Figure 43 provides results of the velocity in the fume hood. The important results are located at the entrance and exit of the mullite tube. These velocities can later be imported into the deposition model as boundary conditions. Figure 44 provides a velocity field in the fume hood. This result provides the direction of the flow through the tube caused by the fume hood.

Figure 44: Arrow Velocity Field of Fume Hood Simulation
Figure 44 also confirms the speculation of entrance and exit through the tube based on the flow. The entrance is confirmed to be the protruding mullite tube and the exit is the side that the stopper can be possible placed on.

Using both figure 43 and 44, the results of the velocity and velocity field are used in the simulation by orientating the tube and inserting the correct initial flow through the tube.

The final boundary conditions needed to be specified is the outlet pressure and the non-slip conditions on the walls and the surfaces.

The outlet boundary has a specific pressure:

\[ p = p_o \]

Where, \( p_o \) is the atmospheric pressure.

The surfaces and walls of the mullite tube and the solution stage have no-slip boundary conditions:

\[ \mathbf{u} = 0 \]

Using the Incompressible Navier-Stokes application model, COMSOL can easily associate the momentum balance and boundary conditions in the idealized geometry of the deposition furnace and deposition solution stage to produce results based on the simulation.
5.5 Energy Transport

The energy balance equation applied to this model considers heat transfer by convection and conduction, despite the use of a radiation furnace, the effect of radiation is neglected. The radiation is neglected in this model because the bulk gas temperature is assumed to change equally with the temperature of the mullite tube and solution stage. The temperature of the deposition experiments do not reach excess of 400°C, therefore, the simulation neglects the effect of radiation initially. The solution stage is initially assumed to be heated by convection and conduction:

\[ \rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (-k \nabla T) + \rho C_p \mathbf{u} \cdot \nabla T = Q \]

Where \( C_p \) denotes the specific heat capacity (J/(kg*K)), \( k \) is the thermal conductivity (W/(m*K)), and \( Q \) is a source term (W/m\(^3\)).

At the inlet and the outlet, a boundary condition of convective flux is used. This assumes all energy passing through is due to convective transport. With the assumption that a negligible amount of reactants leave the reactor the conduction across this boundary is negligible.

\[ q_{\text{cond}} \cdot \mathbf{n} = -k \nabla T \cdot \mathbf{n} = 0 \]
\[ q \cdot \mathbf{n} = \rho C_p T \mathbf{u} \cdot \mathbf{n} \]

At the surface the mullite tube sits directly under the radiation furnace, a temperature boundary condition needs to be specified. The boundary condition is a function of time instead of a constant temperature.

\[ T = T_{\text{furnace}} \]
Where $T_{\text{furnace}}$ is a function developed to model the temperature profile of the deposition furnace. The furnace operates based on a heating profile that is a function of time. The heating profile needs to be modeled. The experimental protocol of the furnace is modeled by recording the temperature and the corresponding time to develop a mathematical heating profile.

An exponential model using an average temperature, initial temperature, a correction factor (alpha), and a typical residence time, as a function of time is developed.

$$
T_{\text{furnace}} = 300 \left( 1 - e^{\left(-\alpha \frac{t}{\tau}\right)} \right) + 298
$$

Where $\alpha$ is the correction factor, $t$ is the time, and $\tau$ is the residence time of the deposition furnace (298 converts Celsius to Kelvin).

The remaining boundary conditions in the deposition furnace are heat fluxes. The walls of the mullite tube will have a heat flux boundary condition. The solution stage will also have a heat flux boundary condition. The deposition furnace readily loses heat to the surroundings.

Using the convection and conduction application model, COMSOL can easily associate the energy balance with the boundary conditions and the model geometry in the idealized geometry of the deposition solution stage to produce results based on the simulation.
5.6 Mass Transport

The mass transfer in the deposition furnace is represented by the convection and diffusion equation:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (D_i \nabla c_i + c_i \mathbf{u}) = R_i$$

Where $D_i$ is the diffusion coefficient (m$^2$/s), and $R_i$ is the reaction term, but there is no reaction in the fluid phase. The equation assumes that the species $i$ is dilute in the bulk gas.

Boundary conditions for mass transport specifies an initial concentration of $A$ at the inlet, in this case, $A$ is zero at the inlet because the solution is evaporated from liquid to vapor during the experiment located on the solution stage.

$$c_i = 0$$

Ideally, the stopper at the end of the mullite tube will allow circulation. This circulation will allow the reactant more time to deposit. This model assumes that the reactant deposits completely without leaving the deposition furnace, therefore, the exit concentration boundary condition is considered negligible.

$$c_i = 0$$

The walls of the mullite furnace and the non-aluminum containing walls of the solution stage have a boundary condition of insulation. This insulation condition states that no mass transport is across these boundaries.
\[ \mathbf{N}_j \cdot \mathbf{n} = 0 \]

Two remaining boundary conditions are the flux of the solution to vapor and the deposition flux onto the aluminum sample.

The flux of the solution vaporizing needs a function to model the relationship to temperature. \( T_{\text{rxn}} \) represents this flux. \( T_{\text{rxn}} \) combines the initial reaction temperature, the peak reaction temperature, and the endpoint reaction temperature into a standard deviation bell curve to describe the normalized heat flux that consists of the vaporization and reaction fluxes (Figure 45).

Figure 45: The Reaction Temperature Flux Relationship Profile

The data is correlated by a function:

\[
f(x) = \frac{e^{-(x-\mu)^2/(2\sigma^2)}}{\sigma \sqrt{2\pi}}
\]
This f(x) multiplied by the total flux achievable is equal to the $T_{\text{rxn}}$, Where $x$ is the temperature, $\mu$ is the average temperature of the experiment, and $\sigma$ is the standard deviation of temperature of the experiment.

The last boundary condition is where the aluminum sample is resting on the solution stage. Until a deposition flux rate is identified this flux is assumed to be a certain flux. In this model it is assumed to be a function of concentration:

$$N_i = -k_i \left( c_{i,\text{Sol}} - c_{i,\text{Gas}} \right)$$

Where $N_i$ is the deposition flux and $c_{i,\text{Sol}}$ and $c_{i,\text{Gas}}$ is the concentration of solution and gas at the deposition surface.

Using the convection and diffusion application model, COMSOL can easily associate the mass balance and boundary conditions to the model geometry in the idealized geometry of the deposition solution stage to produce results based on the simulation.

5.7 Modeling in COMSOL Multiphysics

5.7.1 Incompressible Navier-Stokes

1. Start COMSOL Multiphysics.

2. In the Application Modes list, select Chemical Engineering Module> Momentum Transport>Laminar Flow>Incompressible Navier-Stokes>Transient Analysis.
3. Click **OK**.

### 5.7.2 Geometry Modeling

There are several ways to construct the geometry of the unique deposition furnace. The method used in this research was to construct a model by drawing an object of a correct amount of lines and then going to change the distance between the lines to accurate values.

1. Select from the header **Draw>Draw Objects>Line.**
Figure 47: Drawing the Deposition Furnace

2. Construct two different objects that can represent the furnace and the solution stage.

Figure 48: Inaccurate Geometry of Deposition Furnace
3. Maneuver the solution stamp inside of the deposition furnace.

4. On the draw toolbar, click **Difference**.

![Figure 49: Inaccurate Deposition Furnace and Solution Stage](image)

5. Double-click on the deposition furnace model and insert correct values for the dimensions of the deposition furnace and solution stage in Object Properties:
The final geometry should be:

**Table VII: Dimensions for Accurate Deposition Furnace**

6. Click **OK**.

Curves | \(x_1\) (m) | \(y_1\) (m) | \(x_2\) (m) | \(y_2\) (m) | weight
---|---|---|---|---|---
1 | -0.0047 | 0.004156 | -0.0047 | 0.004906 | 1
2 | -0.0047 | 0.004156 | -2.00E-04 | 0.003831 | 1
3 | -0.0047 | 0.004906 | -2.00E-04 | 0.005231 | 1
4 | -2.00E-04 | 0.003831 | 0.0018 | 0.002531 | 1
5 | -2.00E-04 | 0.005231 | 0.0018 | 0.006531 | 1
6 | 0.0018 | 0.002531 | 0.0053 | 0.002531 | 1
7 | 0.0018 | 0.006531 | 0.0053 | 0.006531 | 1
8 | 0.0053 | 0.002531 | 0.0403 | 0.002531 | 1
9 | 0.0053 | 0.006531 | 0.0403 | 0.006531 | 1
10 | 0.0103 | 0.004031 | 0.0103 | 0.004531 | 1
11 | 0.0103 | 0.004031 | 0.02 | 0.004031 | 1
12 | 0.0103 | 0.004531 | 0.0119 | 0.004531 | 1
13 | 0.0119 | 0.004281 | 0.0119 | 0.004531 | 1
14 | 0.0119 | 0.004281 | 0.01353 | 0.004281 | 1
15 | 0.01353 | 0.004281 | 0.01353 | 0.004531 | 1
16 | 0.01353 | 0.004531 | 0.02 | 0.004531 | 1
17 | 0.02 | 0.004031 | 0.02 | 0.004531 | 1
18 | 0.0403 | 0.002531 | 0.0438 | 0.002531 | 1
19 | 0.0403 | 0.006531 | 0.0438 | 0.006531 | 1
20 | 0.0438 | 0.002531 | 0.0438 | 0.002731 | 1
21 | 0.0438 | 0.002731 | 0.0438 | 0.006331 | 1
22 | 0.0438 | 0.006331 | 0.0438 | 0.006531 | 1
7. If one is unable to achieve this model because of an error, check the amount of lines that are drawn in the original model.

5.7.3 Incompressible Navier-Stokes Physics Subdomain Settings

Start by setting up and solving the equations for the fluid flow through the deposition furnace. Air is the fluid that flows through the furnace.

1. Select the menu item Physics>Subdomain Settings.

2. Select 1 from the Subdomain selection list and load “Air 1 atm” from the library material.
Figure 51: Incompressible Navier-Stokes Subdomain Settings

3. Load the correct functions for the selected library material. Select the menu item **Options>Functions**.
5.7.4 Incompressible Navier-Stokes Boundary Conditions

1. Select the menu item **Physics>Boundary Settings**.

2. Set the following boundary conditions:

<table>
<thead>
<tr>
<th>Settings</th>
<th>Boundary 1</th>
<th>Boundary 20 and 22</th>
<th>All Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boundary type</td>
<td>Inlet</td>
<td>Outlet</td>
<td>Wall</td>
</tr>
<tr>
<td>Boundary condition</td>
<td>Velocity</td>
<td>Pressure</td>
<td>No Slip</td>
</tr>
<tr>
<td>U0 m/s</td>
<td>2</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>p0 Pa</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

Table VIII: Incompressible Navier-Stokes Boundary Conditions
3. Click OK.

5.7.5 Convection and Conduction

1. Select the menu item Multiphysics>Model Navigator.

2. In the Application Modes list, select Chemical Engineering Module>Energy Transport>Convection and Conduction>Transient Analysis.
3. Click the Add button, and then click OK.

5.7.6 Convection and Conduction Physics Subdomain Settings

1. Select the menu item Physics>Subdomain Settings.

2. Select 1 from the Subdomain selection list and load “Air 1 atm” from the library material.
3. Click the **Init** tab and type 298 in the $T(0)$ edit field.

4. Click **OK**.

### 5.7.7 Convection and Conduction Boundary Conditions

1. Select the menu item **Physics>Boundary Settings**.

2. Set the following boundary conditions:

<table>
<thead>
<tr>
<th>Settings</th>
<th>Boundary 1, 20, 22</th>
<th>Boundary 2-7, 18,19, 21</th>
<th>Boundary 8, 9</th>
<th>Boundary 10-13,15-17</th>
<th>Boundary 14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boundary condition</td>
<td>Convective Flux</td>
<td>Heat Flux</td>
<td>Temperature</td>
<td>Heat flux</td>
<td>Heat flux</td>
</tr>
<tr>
<td>TO (K)</td>
<td>-</td>
<td>-</td>
<td>$T_{Furnace}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Inward Heat Flux W/m²</td>
<td>-</td>
<td>-0.01</td>
<td>-</td>
<td>-0.1</td>
<td>-0.5</td>
</tr>
</tbody>
</table>

Table IX: Convection and Conduction Boundary Conditions

3. Click **OK**.
5.7.8 Convection and Diffusion

1. Select the menu item **Multiphysics>Model Navigator**.

2. In the **Application Modes** list, select **Chemical Engineering Module>Mass Transport>Convection and Diffusion>Transient Analysis**.

![Image of Model Navigator Convection and Diffusion]

Figure 56: Model Navigator Convection and Diffusion

3. Click the **Add** button, and then click **OK**.

5.7.9 Options and Settings

1. Select the menu item **Options>Expressions>Scalar Expressions**.

2. Type in the following entries in the **Scalar Expressions** dialog box:
Figure 57: Convection and Diffusion Scalar Expressions

These values come from the kinetic analysis performed with the DSC experiments.

3. Click OK.

5.7.10 Convection and Conduction Physics Subdomain Settings

1. Select the menu item Physics>Subdomain Settings.

2. Select 1 from the Subdomain selection list and type in the following entries:
3. Click OK.

5.7.11 Convection and Diffusion Boundary Conditions

1. Select the menu item **Physics>Boundary Settings**.

2. Set the following boundary conditions:

<table>
<thead>
<tr>
<th>Settings</th>
<th>Boundary 1,20,22</th>
<th>Boundary 14</th>
<th>Boundary 16</th>
<th>All Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boundary condition</td>
<td>Concentration</td>
<td>Flux</td>
<td>Flux</td>
<td>Insulation</td>
</tr>
<tr>
<td>c</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Inward flux</td>
<td>-</td>
<td>T_rxn</td>
<td>-c</td>
<td>-</td>
</tr>
</tbody>
</table>

Table X: Convection and Diffusion Boundary Conditions

3. Click OK.
5.7.12 Post-Processing and Visualization

1. Click the **Plot Parameters** button on the Main toolbar.

2. Go to the **Surface** page and select **Convection and Diffusion** (ched)>**Concentration, c** from the **Predefined quantities** list.

![Post-processing Surface Plot Menu](image)

Figure 59: Post-processing Surface Plot Menu

3. Click **OK**.

5.8 Results

Figure 60 shows the steady-state velocity field in the deposition furnace:
Figure 60: Steady State Velocity field Results in the deposition furnace

The flow is described as steady state because the flow profile becomes developed initially and remains until the completion of the experiment.

Figure 61: Zoomed; Beginning of Experiment Velocity Field Results
Between Figure 61 and 62, the velocity field is comparable and is assumed to initially develop into the final velocity flow.

The flow is shown to develop above and below the solution stage. Slight non-developed flow is shown immediately contacting the solution stage, because of the solution stage interrupting the flow. The majority of the flow tends to have a more distinct developed flow above the solution stage.

The temperature of the deposition furnace changes with time, but at the completion of the experiment the temperature in the furnace is near constant as expected. The Final temperature of this experiment is 598K. The following figure represents the final value, the variations are due to numerical solvers, and the significant figures will round to 598K.
Figure 63: Temperature Distribution Results of the Deposition Furnace

Figure 64: Mid-experiment Temperature of Deposition Furnace
Figure 64 represents the time where the near maximum temperature is met. The furnace then remains at this temperature for the remaining experimental time. The following figure will show the furnace heats fairly uniformly.

Figure 65: 25% Temperature Profile of Deposition Furnace
Figure 66: 10% Experimental Temperature Profile of Deposition Furnace

Shown in figure 65 and 65, the furnace heats the mullite tube uniformly.
Figures 63-67 represent that the mullite tube is heated approximately uniformly by the radiation furnace.

The concentration profile is a significant result from this model. General trends can be drawn from the concentration results coupled with the temperature results.

Initial concentration gradients are zero in the mullite tube. The solution needs to vaporize before concentration can be recorded. Shown in Figure 68, the initial concentration is zero.
Figure 68: Initial Concentration Gradient in the Deposition Furnace

As the solution vaporizes, the concentration gradient appears.
Figure 69: Initial Vaporization of Solution in Deposition Furnace

Figure 69 shows an initial vaporization of the solution in the deposition furnace; later on more solution vaporizes and can be observed to diffuse inside the mullite tube.

![Figure 69](image)

Figure 70: Mid-Experiment Concentration Profile in Deposition Furnace

This figure 70 shows the time where the solution is vaporizing at its maximum flux. This maximum flux vaporizes the solution and allows for deposition to readily occur later in the experiment.

![Figure 70](image)
Figure 71: Concentration Profile Results of the Deposition Furnace

This model provides a steady state value of concentration centrally located over the solution stage and aluminum sample. This can identify an ideal scenario for the deposition to occur by changing the simulation parameters. By changing different heating rates, solution sizes, locations in the mullite tube, these results can provide an ideal solution stage location to be identified.

By changing the location of the solution stage, the steady state concentration profile according to the location in the deposition furnace shows an ideal solution stage.
Figure 72: Multiple Solution Stage Location Concentration Results

Figure 72 identifies that changing the location of the solution stage will alter the rate and extent of solution that vaporizes and ultimately deposits onto the aluminum sample. From this result, it can be shown that the ideal location is directly under the furnace in the middle and front of the deposition furnace. This conclusion is made by Figure 72. The figure graphically shows the tube with the largest amount of maximum concentration being vaporized. From the graph, it can be seen that the tube with the largest amount of concentration being expelled by the solution stage is the mullite tube with the solution stage most directly located in the middle and front of the radiation furnace.
CHAPTER VI

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

6.1 Summary
A protocol to analyze deposition reaction kinetics using conventional DSC was formulated in this research. Preliminary modulated DSC analysis seemed to indicate the potential to improve experimental repeatability. This research outlines the experimental procedure to analyze deposition reactions via conventional DSC, and the corresponding data analysis procedure to extract reaction kinetics parameters is demonstrated.

Previous experimental studies showed that a reproducible protocol to produce results consisted of a 1 µL sample with the experiment initiated at 200°C and then progressing at a heating rate of 2.5 °C/min to 400°C. Kinetic Analysis was performed using the DSC runs that detected reactions through this experimental protocol.

The present work differentiates itself from the previous work in several ways:

1. One of the fundamental differences is the use of the DSC instead of the TGA, i.e. a non-isothermal process. Steady state will not be achieved in DSC experiments, and an analysis of dynamic data must be implemented. As demonstrated by (Nagarajan et al., 2006), who utilized TGA to perform
isothermal deposition experiments. She assumed a reaction order to analyze the data and required multiple experiments to extract the temperature-dependent parameters. Namely, this experimental data can be shown to follow the constant volume non-isothermal batch reactor model. Indeed, the design equations can be manipulated as follows:

\[- \frac{dC_A}{dt} = r_A \quad (1)\]

With,

\[r_A = -kC_A^n\]

And

\[k_{(T)} = k_{(T^0)} \exp\left(\frac{-E}{R}\left(\frac{1}{T} - \frac{1}{T^0}\right)\right)\]

\[C_A = C_A^0(1 - x_A)\]

Therefore, Equation (1) can be linearized as:

\[\ln \left( \frac{dx_A}{dt} \right) = \ln Z - \left( \frac{E}{R} \right) \left( \frac{1}{T} - \frac{1}{T^0} \right) + n \ln(1 - x_A)\]

\[Z = k_{(T^0)} \left( C_A^0 \right)^{n-1}\]

With,

This course of methodology can extract all the parameters, namely the activation energy, reaction order, and reaction rate constant from a single experiment. Isothermal experiments required several runs to extract these parameters. In addition, to refine the assumption of the reaction order isothermal experiments needed an assumption of the reaction order. Current
research using the DSC non-isothermal experiments allows the reaction order not to be assumed.

Using the differential method of analysis of batch reactors, the reaction kinetics are extracted from experimental DSC data. The Borchardt and Daniels method is implemented to extract conversion data from the DSC data. Continuing to use the design equations manipulated in the Chapter 3, least squares method is implemented to extract reaction order, activation energy, and the reaction rate constant with the corresponding errors associated with each parameter. Kinetic analysis results are available in Chapter 4.2.

2. Another key difference is that while films grown on iron-based substrates have a thickness ranging between 100-300 nm; in the current research much thinner (<50nm) protective coatings are deposited on non-iron substrates. These thin films are examined through DSC analysis to extract important reaction kinetic parameters.

3. This research successfully demonstrated that the deposition process can be characterized via DSC experiments. Further studies can now be used towards furthering scale-up criteria and extracting detailed kinetic characterization of coating technologies leading to conversion and protective coatings.

4. This research successfully demonstrated that a laboratory-scale deposition environment can be simulated via finite element modeling (COMSOL). Future simulations are anticipated to expand a simplified 2D model into a more realistic 3D model. This simulation and future simulations will be used in
experimental design to the laboratory deposition furnace leading to scale-up criteria and detailed kinetic characterization of coating technologies leading to conversion and protective coatings. Numerical Simulation results are listed in chapter 5.8.

6.2 Conclusions
This research successfully incorporated the use of a DSC in the study of a CVD mechanism by extracting batch reactor kinetic parameters. The research focused on the conventional heating rate but included preliminary analysis using modulation. A successful protocol has been developed to perform DSC experiments, extract heat flow data, manipulate heat flow to conversion, and then extract reactor kinetic parameters. Multiple experiments have been used to test for reproducibility.

The DSC experiments incorporate a significant amount of inconsistency. Similar experiments are observed to behave differently. The majority of experiments revealed no reaction. The experiments used in this research were taken on the same day and are assumed to berepeatable. These experiments are only a select amount of the total amount of experiments run throughout the two years of this thesis work.

This research successfully developed an initial simulation of a deposition furnace. The deposition furnace is modeled using basic assumptions, and can be expanded into a 3D fully functional sophisticated model. This research proved initial assumptions of the results from the simulation. The results were that the flow created through the mullite tube was developed and the optimum position inside the mullite tube is directly under the furnace to observe optimum accurate heating profiles.
6.3 Recommendations

An analysis needs to be performed identifying why certain experiments exhibit reactions while identical experiments do not. Key analysis may be targeted to sample size, gas flow rate, pan type, solution homogeneity, room pressure, and humidity. A future useful experiment, if possible, may consist of using a video recording device, recording a hermetic pan and varying solution sizes in the radiation furnace. This experiment will observe a potential rupture in the seal or not.

The gas flow rate may have some impact on the pinhole pans. Increasing flow rates will increase the pressure over the pinhole and affect the rate at which reactants leave the reaction environment. Careful must be taken during the low flow rate in the DSC because this flow is aimed at keeping moisture away from the cell and prevent any potential damage of the instrument.

A continuously stirred solution vials may create a more homogeneous solution than current solutions. The lack of homogeneity in each solution may have a drastic affect on the reaction taking place or not. Creating a more homogeneous solution may allow truly comparable experiments. Without a true homogeneous solution, the true amount of iron acetate in solution will change depending on the time of the sample.

The last recommendation is to enhance the kinetic analysis MATLAB program. Instead of having the user enter the reaction temperature limits, the program should automatically determine them and create a linear baseline itself. Further alterations need to create the kinetic analysis program more user-friendly.
REFERENCES


APPENDICIES
APPENDIX A:

Kinetic Analysis Matlab Program

% kinetic_analysis.m
%Combination of Filtering, Plotting, and Finding Xa versus T plot
%Uses Data with Reaction, user adds baseline by slope.

% Reading and filtering DSC Data
% Nano-coatings on Metallic Substrates
% Spring 2010
%
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%
% Last Revision: 04/12/10

clear;
% cleanup (clear) fields
clc;

% We can read data directly from MS Excel
[DataFile, TextData, RawData] = ...
xlsread('extracted experiments.xls', 'Linear_1uL_A');

% classify data
times(:,1) = DataFile (:,1);
Ts(:,1) = DataFile (:,2);
Ws(:,1) = DataFile (:,3);

% classify data
timeb(:,1) = DataFile (:,1);
Tb(:,1) = DataFile (:,2);
Wb(:,1) = (0.0106664981*Ts(:,1) - 0.8069240913); %1 - xA(:,1);

subplot(1,1,1), plot (Tb, Wb, 'b:');
hold on;

subplot(1,1,1), plot (Ts, Ws, 'k:');

xlabel ('Temperature, T [°C]');
ylabel ('Differential Heat, W [W g^{-1}]');
legend ( 'Baseline', 'Sample');
title ('Raw Data');
grid;

hold off;

% fprintf ('n Press <Enter> to continue ...');
% pause;

% before we can proceed, we need
% to “weed out” repeated points

nsig = 5;
% I wrote a program to do that ...
% see filter_jeg

% baseline
[Tb1 Wb1] = filter_jeg (nsig, Tb, Wb);
% sort arrays
Dbf = [Tb Wb];
Dbf_sorted = sortrows (Dbf);

% pause;

clear Tb1 Wb1
Tb1 = Dbf_sorted(:,1);
Wb1 = Dbf_sorted(:,2);

% Sample
[Ts1 times1] = filter_jeg (nsig, Ts, times);
[Ts1 Ws1] = filter_jeg (nsig, Ts, Ws);
% sort arrays
Dsf = [Ts Ws1];
Dsf_sorted = sortrows (Dsf);

% pause;

clear Ts1 Ws1
Ts1 = Dsf_sorted(:,1);
times1 = Dsf_sorted(:,2);
Ws1 = Dsf_sorted(:,3);
% plot results to check
subplot(1,1,1), plot (Tb1, Wb1, 'b:');
hold on;

subplot(1,1,1), plot (Ts1, Ws1, 'k:');
xlabel ('Temperature, T [°C]');
ylabel ('Differential Heat, W [W g^{-1}]');
legend ('Baseline', 'Sample');
title ('Filtered Data - Phase 1');
grid;
hold off;

%fprintf ('\n Press <Enter> to continue ...');
pause(5);

% filter again
[Tbf Wbf] = filter_jeg (nsig, Tb1, Wb1);
[Tsf Wsf] = filter_jeg (nsig, Ts1, Ws1);
[Tsf timesf] = filter_jeg (nsig, Ts1, times1);

% plot results to check
subplot(1,1,1), plot (Tbf, Wbf, 'b:');
hold on;

subplot(1,1,1), plot (Tsf, Wsf, 'k:');
xlabel ('Temperature, T [°C]');
ylabel ('Differential Heat, W [W g^{-1}]');
legend ('Baseline', 'Sample');
title ('Filtered Data - Phase 2');
grid;
hold off;

%fprintf ('\n Press <Enter> to continue ...');

% pause;

Ns = length(Wsf);
Nb = length(Wbf);
N = min(Nb, Ns);

% Tlow = max(Tbf(1), Tsf(1));
% Thigh = min(Tbf(Nb), Tsf(Ns));

% ADJUST FOR EACH PART%
% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
Tlow = 295.5;
Thigh = 367;
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% %LINEARIZED
% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Tlow = 299.4325;
% Thigh = 345.5318;
% % % % % % % % % % % % % % % % % % % % % % % % % % % % %

% filter the data
M = 501;

Ti = linspace (Tlow, Thigh, M);
Ti = Ti';

% 'Method' specifies alternate methods.
% The default is linear interpolation. Use an empty matrix [] to specify
% the default. Available methods are:
% % 'nearest' - nearest neighbor interpolation
% 'linear' - linear interpolation
% 'spline' - piecewise cubic spline interpolation (SPLINE)
% 'pchip' - shape-preserving piecewise cubic interpolation
% 'cubic' - same as 'pchip'
% 'v5cubic' - the cubic interpolation from MATLAB 5, which does not
% extrapolate and uses 'spline' if X is not equally
% spaced.

method = 'spline';
Wis = interp1(Tsf, Wsf, Ti, method);  
tis = interp1(Tsf, timesf, Ti, method);  
Wib = interp1(Tbf, Wbf, Ti, method);

% plot interpolated data
subplot(1,1,1), plot (Ti, Wib, 'b:', Ti, Wis, 'r:');
xlabel ('Temperature, T [^oC]');
ylabel ('Differential Heat, W [W g^-1]');
legend ('Baseline', 'Sample');
title ('Truncated/Interpolated Data');
grid;

% fprintf ('\n Press <Enter> to continue ...');
% pause;

Wdiff = zeros(size(Wib));
Wdiff = Wis - Wib;

for i = 1:size(Wib)
    if Wdiff <0
        Wdiff(i) =0;
    end
end

Tdiff = Ti;
% end
hold off;

subplot(1,1,1), plot (Tdiff, Wdiff, 'r:');
xlabel ('Temperature, T [^oC]');
ylabel ('Differential Heat, W [W g^{-1}]');
grid;

fprintf ('n Press <Enter> to continue ...');
pause;

extract Heat of Reaction
% Be careful here !!!
% You need to isolate the subset (T, W) that
% corresponds to the reaction of interest!!!
DHrxn = trapz(Tdiff, Wdiff);

%Get Table of Conversions%

% simpler this way
xA = cumtrapz(Tdiff, Wdiff)/DHrxn;

subplot(2,1,1), plot (Tdiff, xA, 'k:');
xlabel ('Temperature, T [^oC]');
ylabel ('Conversion, x_A');
grid;

% For this plot you need the original data
% I added a few lines in the filtering section

% Plot Conversion (xA) vs. time (t)

subplot(2,1,2), plot (tis/60, xA, 'k:');
xlabel ('time, t [min]');
ylabel ('Conversion, x_A');
grid;

% fprintf ('n Press <Enter> to continue ...');
% pause;

% Kinetic Analysis % Once it is in 1 Matrix it will easy.
% Y = a + b X + c X^2

% ln dXa/dt = ln k0 + (n-1)Ca0 + n ln(1-Xa) + (-E/R)[1/TXa + 1/TXao]

% Y = ( a ) + b (X1) + (c) (X2)

% find the time derivative for the conversion
N = length(xA);
DeltaxA = zeros(N-1,1);
Deltat = zeros(N-1,1);
DeltaxA = xA(2:N) - xA(1:N-1);
Deltat = tis(2:N) - tis(1:N-1);
Deltat = Deltat/60;

dxAdt = DeltaxA./Deltat;
% find half-way Temperature and Conversion
thalf = (tis(2:N) + tis(1:N-1))/2;
Thalf = (Td(2:N) + Td(1:N-1))/2;
xAhalf = (xA(2:N) + xA(1:N-1))/2;

% plot results (for verification purposes only)
subplot(1,1,1), semilogy(thalf/60, dxAdt, 'rs:', ...
   thalf/60, Thalf, 'b^:', thalf/60, xAhalf, 'mo');
grid;
legend('time derivative of conversion', ...
   'half-way Temperature, [^oC]', ...
   'half-way conversion, x_A');
xlabel(' time, t [min]');

% fprintf ('n Press <Enter> to continue ...');
% pause;

N1 = 1;
N2 = N-1;
loop = 1;

while (loop > 0)

% initialize
y = [ ];
x1 = [ ];
x2 = [ ];
y_fit = [ ];
y_fitu = [ ];
y_fitl = [ ];

counter = 0;
% ln dXa/dt = ln k0 + (n-1)Ca0 + n ln(1-xAhalf) + (E/R) [-1/Thalf + 1/To]
% Y = ( a ) + b (X1) + (c) ( X2)

% find suitable reference
Tref = median(Thalf) + 273.15;
for i = N1:N2
   if ((dxAdt(i) > 0) && (xAhalf(i) < 1)) && (xAhalf(i) > 0)
      y = [y ; log(dxAdt(i))];
      x1 = [x1; log(1-xAhalf(i))];
      x2 = [x2; 1/Tref - 1/(Thalf(i)+273.15)];
   end
end

ident = ones(size(y));
Jacobian = [ident, x1, x2];

Covariance = inv(Jacobian' * Jacobian);
b = Jacobian' * y;

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% check the difference between 'mldivide' and 'inv'
a = (Jacobian' * Jacobian)b;

% echo on
% ln dxA/dt = [ln k0 + (n-1)CA0] + n [ln(1-xAhalf)] + (E/R) [-1/Thalf + 1/To]
% Y = Yo + n [x1] + (E/R) [x2]

n = a(2);
Yo = a(1);
EoverR = a(3);
y_fit = Jacobian*a;

% finding the errors
df = length(y)-length(a);
risk = 0.05; % 5% risk-level, or 95% confidence
e = y_fit - y;
s2 = e'*e;
s2 = s2 / df;

% fixed for the time being
% t = 2.5;
% substituted for the actual t
% 04/11/10
t = t_stud (risk, df);

Cov = inv(Jacobian'*Jacobian);
Ea = zeros(size(a));
for ia = 1:length(a)
    Ea(ia) = sqrt(Cov(ia,ia)*s2)*t;
end

fprintf('n *** Parameters ***

 t intercept   (Yo) t = %12.3g +/- %12.3g (%7.3g %%)', ... a(1), Ea(1), abs(Ea(1)/a(1)*100));
fprintf(' t order of rxn (n) t = %12.3g +/- %12.3g (%7.3g %%)', ... a(2), Ea(2), abs(Ea(2)/a(2)*100));
fprintf(' t activation energy (E/R), K t = %12.3g +/- %12.3g (%7.3g %%)', ... a(3), Ea(3), abs(Ea(3)/a(3)*100));

% find confidence intervals
y_fitu = Jacobian*(a+Ea);
y_fitl = Jacobian*(a-Ea);
En = Ea(2);

% where Xa = partial Hrxn/ total Heat of Rxn
% R = 8.3145 J/K*mol universal gas constant
% Ca0 = initial concentration = known from data.
% E = activation energy = unknown
% n = reaction parameter = unknown  
% T, To = temp and intial temp = known from data.  
% Z = grouping of constants, mainly ko the reaction rate constant. 

%%% LINEARIZING DATA %%%% 
% initialize  
y_l = [];  
x1_l = [];  
x2_l = [];  
x3_l = [];  
y_fit_L = [];  

counter = 0;  

% ln dxA/dt = [ln k0 + (n-1)CAo] + n [ln(1-xAhalf)] + (E/R) [-1/Thalf + 1/To]  
% Y = Yo + n [x1] + (E/R) [x2]  
% Y - n * x1 = Yo + (E/R) x2  

for i = 1:N  
    if ((dxAdt(i) > 0) && (xAhalf(i) < 1)) && (xAhalf(i) > 0)  
        y_l = [y_l ; log(dxAdt(i))];  
        x1_l = [x1_l; log(1-xAhalf(i))];  
        x2_l = [x2_l; 1/Tref - 1/(Thalf(i)+273.15)];  
        x3_l = [x3_l; log(dxAdt(i)/(1-xAhalf(i))^n)];  
    end  
end  

y_fit_L = y_fit - n * x1;  
y_fit_Lu = y_fitu - (n-En) * x1;  
y_fit_Ll = y_fitl - (n+En) * x1;  

%%% LINEARIZING DATA PLOT %%%% 

subplot(1,1,1), plot (x2_l, x3_l, 'bo', ... 
    x2, y_fit_L, 'r--', ... 
    x2, y_fit_Lu, 'r:', ... 
    x2, y_fit_Ll, 'r:');  

% subplot(1,1,1), plot (x2_l(35:180), x3_l(35:180), 'r:'); Cutting without  
% Cutting Data  

xlabel ('[1/T - 1/To]');  
ylabel ('ln [(dXa/dt)/(1 - Xa)^n]');  
grid;  

answer = input ('\n do you want to try again? (y>0 n<0)');  
if answer > 0  
    fprintf ('\n Currently using : from %7i to %7i \n', N1, N2);
% yN1 = input (' Enter y(N1): '); 
% yN2 = input (' Enter y(N2): '); 

yN1 = min([y_fit_L; y_fit_LL; y_fit_Lu]); 
yN2 = max([y_fit_L; y_fit_LL; y_fit_Lu]); 

low = (x3_l <= yN1); 
high = (x3_l <= yN2); 

N1 = sum(low); 
N2 = sum(high); 

fprintf ('\n Now using : from %7i to %7i \n', N1, N2); 

loop = 1; 
else 
    loop = -1; 
end 
end 

%SUCCESS = XLSWRITE('c:\matlab\work\myworkbook.xls','A2:C4') 

% We can write data directly to MS Excel 

% ATTEMPT = XLSWRITE('writeA.xls', y_l,'y_l'); 
% ATTEMPT1 = XLSWRITE('writeA.xls', x1_l,'x1_l'); 
% ATTEMPT2 = XLSWRITE('writeA.xls', x2_l,'x2_l'); 
% ATTEMPT3 = XLSWRITE('writeA.xls', x3_l,'x3_l'); 
% write data 
% DataFile (:,1) = y_l(:,1); 
% DataFile (:,2) = x1_l(:,1); 
% DataFile (:,3) = x2_l(:,1); 
% DataFile (:,4) = x3_l(:,1);
APPENDIX B:

FILTERING IMPORTANCE

Data filtering results of a DuPont DSC experiment are presented next.

![Figure 1B: DuPont DSC Raw Experimental Data](image1)

Figure 1B: DuPont DSC Raw Experimental Data

Shown in figure 1B, the raw data exhibits extreme fluctuations between data points. These fluctuations are what is considered “noise”. Noise consists of fluctuations in data that are untrue and due to the surroundings of the equipment’s environment.

![Figure 2B: Filtered Data After One Pass](image2)

Figure 2B: Filtered Data After One Pass
The filtering program smoothes the data based on a sensitivity analysis and can be seen through figure 3B compared to figure 1B. The noise is still present, but has decreased from the raw data.

Figure 3B: Filtered Data After Two Passes
APPENDIX C:

FILTER Data Program

% function filter.m

function [xf, yf] = filter_jeg (nsig, x, y)

% this function eliminates repeated values of
%   the dependent variable (x)

xf = []; yf = [];

% constants
small = 1.e-07;
% define significance of filter
%nsig = 6;
epsilon = 0.5 * (10^(-nsig-1));

N = length(x);

% initialize counters & arrays
k = 0;
is = 1;

for i = 1:N-1

   if is < 2 % initialize
      sumx = x(i);
      sumy = y(i);
   end
% using average
delta = abs( x(i) - sumx/is ) / ( small + abs(sumx/is) );

% using point value
%   delta = abs( x(i+1) - x(i) ) / ( small + abs(x(i)) );

%   fprintf ('\n %12.3e \t %12.3e', x(i), delta);

if delta <= epsilon % below significance
    sumx = sumx + x(i+1);
    sumy = sumy + y(i+1);
    is = is + 1;
elseif delta > epsilon | i == N - 1 % above significance, new point
    k = k + 1;
    % average
    xf = [xf; sumx/is];
    yf = [yf; sumy/is];

    %   % point value
    %   xf = [xf; x(i)];
    %   yf = [yf; y(i)];

    is = 1;

%   fprintf ('\n %4i \t %12.3e \t %12.3e', k, xf(k), yf(k));
%   pause(2);

end

end

return;
### APPENDIX D:

#### Current Mass and Volume Calculations

<table>
<thead>
<tr>
<th></th>
<th>MW</th>
<th>Density g/ml</th>
<th>total volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Durad</td>
<td>512</td>
<td>1.124</td>
<td>25</td>
</tr>
<tr>
<td>Iron 2 Acetate</td>
<td>173.94</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **mass durad**: 28.1 g
- **Moles durad**: 5.49E-02 mol
- **volume durad**: 25 ml

<table>
<thead>
<tr>
<th></th>
<th>1%</th>
<th>1.50%</th>
<th>2%</th>
<th>2.50%</th>
<th>3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles Iron(II)Ac</td>
<td>5.54E-04</td>
<td>8.36E-04</td>
<td>1.12E-03</td>
<td>1.41E-03</td>
<td>1.70E-03</td>
</tr>
<tr>
<td>mass Iron (II)Ac</td>
<td>9.64E-02</td>
<td>1.45E-01</td>
<td>1.95E-01</td>
<td>2.45E-01</td>
<td>2.95E-01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>3.50%</th>
<th>4%</th>
<th>4.50%</th>
<th>5%</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.99E-03</td>
<td>2.29E-03</td>
<td>2.59E-03</td>
<td>2.89E-03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.46E-01</td>
<td>3.98E-01</td>
<td>4.50E-01</td>
<td>5.02E-01</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX E:

Previous Research Formulation of Solutions:

<table>
<thead>
<tr>
<th>Solution</th>
<th>Mole% aryl phosphate, percent</th>
<th>Mole% iron additive, anhydrous, percent</th>
<th>Iron Additive, anhydrous, grams</th>
<th>Solvent, grams</th>
<th>Aryl phosphate, grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:10000</td>
<td>99.99</td>
<td>0.01</td>
<td>0.00115</td>
<td>32.7</td>
<td>47.4</td>
</tr>
<tr>
<td>1:1000</td>
<td>99.9</td>
<td>0.1</td>
<td>0.0115</td>
<td>32.7</td>
<td>47.4</td>
</tr>
<tr>
<td>1:100</td>
<td>99.0</td>
<td>1.0</td>
<td>0.115</td>
<td>32.7</td>
<td>47.4</td>
</tr>
<tr>
<td>1:20</td>
<td>95.2</td>
<td>4.8</td>
<td>0.575</td>
<td>32.7</td>
<td>47.4</td>
</tr>
<tr>
<td>1:10</td>
<td>90.9</td>
<td>9.1</td>
<td>1.150</td>
<td>32.7</td>
<td>47.4</td>
</tr>
<tr>
<td>1:5</td>
<td>83.3</td>
<td>16.7</td>
<td>2.300</td>
<td>32.7</td>
<td>47.4</td>
</tr>
<tr>
<td>1:4</td>
<td>80.0</td>
<td>20.0</td>
<td>2.875</td>
<td>32.7</td>
<td>47.4</td>
</tr>
<tr>
<td>1:3</td>
<td>75.0</td>
<td>25.0</td>
<td>3.833</td>
<td>32.7</td>
<td>47.4</td>
</tr>
<tr>
<td>1:2</td>
<td>66.7</td>
<td>33.3</td>
<td>5.750</td>
<td>32.7</td>
<td>47.4</td>
</tr>
<tr>
<td>1:1</td>
<td>50.0</td>
<td>50.0</td>
<td>11.500</td>
<td>32.7</td>
<td>47.4</td>
</tr>
</tbody>
</table>
APPENDIX F:

Calculation of Reaction Rate Constant with varying mole concentrations:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>sample Mass (g)</th>
<th>Sample mol</th>
<th>Reaction Temp C</th>
<th>Pressure (kPa)</th>
<th>To (K)</th>
<th>R L*kPa/(mol K)</th>
<th>MW (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.28E-03</td>
<td>2.49E-06</td>
<td>295.5</td>
<td>101.325</td>
<td>568.65</td>
<td>8.314</td>
<td>512</td>
</tr>
<tr>
<td>B</td>
<td>1.36E-03</td>
<td>2.66E-06</td>
<td>325</td>
<td>101.325</td>
<td>598.15</td>
<td>8.314</td>
<td>512</td>
</tr>
<tr>
<td>C</td>
<td>1.07E-03</td>
<td>2.09E-06</td>
<td>304.1</td>
<td>101.325</td>
<td>577.25</td>
<td>8.314</td>
<td>512</td>
</tr>
<tr>
<td>D</td>
<td>1.79E-03</td>
<td>3.50E-06</td>
<td>338.2</td>
<td>101.325</td>
<td>611.35</td>
<td>8.314</td>
<td>512</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>y</th>
<th>Cao mol/L</th>
<th>Cao mol/m3</th>
<th>ko (L/mol)</th>
<th>ko (L/mol)</th>
<th>ko (m3/mol)</th>
<th>ko (m3/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.021</td>
<td>21.432</td>
<td>1.75</td>
<td>1.97</td>
<td>10.19</td>
<td>10.34</td>
</tr>
<tr>
<td>1</td>
<td>0.020</td>
<td>20.375</td>
<td>7.92</td>
<td>9.28</td>
<td>7.92</td>
<td>8.08</td>
</tr>
<tr>
<td>1</td>
<td>0.021</td>
<td>21.113</td>
<td>6.91</td>
<td>24.96</td>
<td>4.89</td>
<td>3.14</td>
</tr>
<tr>
<td>1</td>
<td>0.020</td>
<td>19.935</td>
<td>9.13</td>
<td>9.02</td>
<td>14.92</td>
<td>16.45</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>y</th>
<th>Cao mol/L</th>
<th>Cao mol/m3</th>
<th>ko (L/mol)</th>
<th>ko (L/mol)</th>
<th>ko (m3/mol)</th>
<th>ko (m3/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>0.015</td>
<td>15.002</td>
<td>1.60</td>
<td>1.81</td>
<td>9.31</td>
<td>9.49</td>
</tr>
<tr>
<td>0.7</td>
<td>0.014</td>
<td>14.262</td>
<td>7.92</td>
<td>9.35</td>
<td>7.92</td>
<td>8.14</td>
</tr>
<tr>
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