HIGH TEMPERATURE HETEROGENEOUS REACTION KINETICS
AND MECHANISMS OF TUNGSTEN OXIDATION

A Dissertation in
Mechanical Engineering

by

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ABSTRACT

Tungsten, which is a material used in many high temperature applications, is limited by its susceptibility to oxidation at elevated temperatures. Although tungsten has the highest melting temperature of any metal, at much lower temperatures volatile oxides are formed during oxidation with oxygen containing species. This differs from many heterogeneous oxidation reactions involving metals since most reactions form very stable oxides that have higher melting or boiling points than the pure metal (e.g., aluminum, iron). Understanding heterogeneous oxidation and vaporization processes may allow for the expansion and improvement of high temperature tungsten applications.

In order to increase understanding of the oxidation processes of tungsten, there is a need to develop reaction mechanisms and kinetics for oxidation processes involving oxidizers and environmental conditions of interest. Tungsten oxidation was thoroughly studied in the past, and today there is a good phenomenological understanding of these processes. However, as the design of large scale systems increasingly relies on computer modeling there becomes a need for improved descriptions of chemical reactions. With the increase in computing power over the last several decades, and the development of quantum chemistry and physics theories, heterogeneous systems can be modeled in detail at the molecular level. Thermochemical parameters that may not be measured experimentally may now be determined theoretically, a tool that was previously unavailable to scientists and engineers. Additionally, chemical kinetic modeling software is now available for both homogeneous and heterogeneous reactions.

This study takes advantage of these new theoretical tools, as well as a thermogravimetric (TG) flow reactor developed as part of this study to learn about mechanisms and kinetics of tungsten oxidation. Oxidizers of interest are oxygen \((O_2)\), carbon dioxide \((CO_2)\), water \((H_2O)\), and other oxidizers present in combustion and energy systems. The primary application for this research topic is the migration of erosion processes in solid rocket motor nozzles. Since oxidation is the primary erosion mechanism of tungsten based nozzles, mitigation of this process through improved comprehension of the chemical mechanisms will increase performance of future rocket systems.
In this dissertation, results of the high temperature reaction rates of bulk tungsten are studied using TG analysis in oxidizing atmospheres of $O_2$, $CO_2$, and $H_2O$ using helium ($He$) as an inert carrier gas. Isothermal reaction rates were determined at temperatures up to 1970 K, and oxidizing species partial pressures up to 64.6 torr. Kinetic parameters such as activation energies, frequency factors, and pressure exponents were determined for each reactive system. An important contribution of this work was quantifying the effects of carbon monoxide ($CO$) on the $CO_2$ reaction, and hydrogen ($H_2$) on the $H_2O$ reaction. In both cases the non-oxidizing species significantly reduced oxidation rates. Results have led to new interpretations and thought processes for limiting nozzle erosion in rocket motors. Combined with the TG analysis, as well as recent theoretical interpretations of reaction thermodynamics and kinetics, a new mechanism for tungsten and $O_2$ oxidation has been developed using a one-dimensional numerical model of the TG flow reactor. Important chemical processes and species are also identified for reaction systems involving $H_2O$ and $CO_2$. In the future, additional studies are needed to improve our understanding of these chemical species and processes so that more advanced kinetic mechanisms may be developed.

In addition to a detailed analysis of high temperature tungsten corrosion processes, synthetic graphite corrosion processes are studied in detail as well. Details of these studies are presented in an attached appendix of this dissertation. These studies considered not only oxidation processes, but decomposition of synthetic graphite in the presence of reducing and inert gas environments.
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NOMENCLATURE

Symbols

\( A \)  
Area; Arrhenius pre-exponential factor

\( c \)  
Concentration of gas-phase species

\( D \)  
Diameter; Diffusion coefficient

\( d \)  
Diameter

\( E \)  
Activation Energy

\( E_a \)  
Apparent activation energy

\( G \)  
Gibbs free energy

\( \dot{g} \)  
Mass consumption rate

\( H \)  
Enthalpy

\( k \)  
Kinetic rate constant; Mass transfer coefficient

\( k_B \)  
Boltzmann’s constant

\( L, l \)  
Length

\( m \)  
Mass

\( \dot{m} \)  
Mass flow rate

\( MW \)  
Molecular weight

\( N \)  
Diffusive mass flux per unit area

\( N_A \)  
Avogadro’s number

\( n \)  
Pressure exponent; site fraction of species

\( n_t \)  
Total number of moles

\( P \)  
Pressure

\( p \)  
Steric factor

\( Q \)  
Heat of combustion

\( q \)  
Molecular flux

\( Re \)  
Reynolds number

\( Ru \)  
Universal gas constant

\( R_c \)  
Recession rate

\( r \)  
Radius

\( \dot{i}_{b-g} \)  
Heterogeneous reaction rate [units of \( b / (cm^2-s) \)]

\( S \)  
Entropy

\( \dot{S} \)  
Surface molar production rate [mol/cm²]

\( s \)  
Sticking coefficient

\( T \)  
Temperature

\( t \)  
Time

\( V \)  
Volume

\( v \)  
Velocity

\( Y \)  
Mole fraction

\( Z \)  
Collision frequency
Greek

λ  Stoichiometric factor
μ  Viscosity
ρ  Density
ε  Energy of interaction
Ω  Collision integral
σ  Number of surface sites occupied; Molecular collision diameter
Γ  Surface site density

Subscripts

a  Adsorption
b  Bulk phase
cr  Crystalline solid phase
D,d  Diameter
g  Gas phase
i  Species \(i\)
j  Species \(j\)
k  Species \(k\); indexing number
L  Length
s  Surface species
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Chapter 1

INTRODUCTION

Tungsten ($W$) has long been a material of interest in high temperature systems. Its high melting and boiling points, density, and high strength make it an interesting candidate for various applications. Tungsten is of particular interest in energy related systems, where heat is used as a driving force to produce usable energy (e.g., engines, reactors, rockets, etc.). However, as with many metals, it is susceptible to oxidation or corrosion at relatively moderate temperatures in comparison with its melting and boiling points. This drawback has limited the application of tungsten. Environments in which tungsten may be utilized have been restricted to vacuums, inert or reducing gases, or conditions where components are engineered with corrosion anticipated and accounted for. Using experimental and theoretical analysis, improved understanding of these reactions will allow the development of a reaction mechanism that may expand the applications of tungsten and other refractory materials, as well as improve existing systems utilizing tungsten.

Development of heterogeneous chemical reaction mechanisms and kinetics – rates of change of chemical species concentrations – for high temperature tungsten oxidation will aid research involving tungsten-based materials and improve the fundamental understanding of surface and gas-phase reactions. Unlike homogenous gas-phase reaction kinetics, heterogeneous reactions are less understood, and much more difficult to predict. Heterogeneous tungsten reactions are of great importance in many chemical processes; of particular interest are corrosion and combustion.

1.1 Motivation

At a fundamental level, developing an understanding of heterogeneous oxidation mechanisms and kinetics of tungsten and other refractory metal surfaces is the primary motivation of the current work. There are several fields in which new knowledge may be applied, particularly in aerospace and defense related applications. Although tungsten and
other refractory metals possess many properties applicable to high temperature environments (see Table 1-1), technological innovations in materials science and chemistry have not overcome issues of material corrosion due to oxidation. A phenomenological understanding of metal oxidation has been known for decades; however, a detailed knowledge of the oxidation process, as well as the effects of multi-component gas-phase systems is not known. A more complete understanding of solid surface and gas-phase interaction and kinetics may provide the required tools to develop innovative approaches for overcoming these corrosion problems. Detailed chemical reaction mechanisms would also provide a means of assessing inclusions of refractory metals into high temperature environments.

Tungsten is currently used as a material for rocket motor nozzles; however, its use has been limited due to its high density and chemical erosion rate (i.e., corrosion or oxidation rates) with certain propellants. Rocket motor nozzles are highly engineered components that are designed to produce maximum thrust and reliability. Small increases in throat area due to corrosion may cause significant reductions in overall performance. In order to increase performance of rocket motors, future systems are expected to operate at greater temperatures and much higher pressure, increasing the physical and chemical strain on nozzles. For this reason there is significant interest in better understanding the chemical processes which lead to tungsten nozzle erosion, so that further increases in erosion rates are avoided or even reduced in forthcoming motor designs.

Table 1-1: Properties of refractory metals (in order of decending melting points).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Density [g/cm³]</th>
<th>Atomic Weight</th>
<th>Melting Point [°C]</th>
<th>Boiling Point [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten (W)</td>
<td>19.3</td>
<td>183.84</td>
<td>3422</td>
<td>5555</td>
</tr>
<tr>
<td>Rhenium (Re)</td>
<td>20.8</td>
<td>186.2</td>
<td>3185</td>
<td>5596</td>
</tr>
<tr>
<td>Tantalum (Ta)</td>
<td>16.4</td>
<td>180.9</td>
<td>3017</td>
<td>5458</td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>10.2</td>
<td>95.9</td>
<td>2623</td>
<td>4639</td>
</tr>
<tr>
<td>Niobium (Nb)</td>
<td>8.57</td>
<td>92.9</td>
<td>2477</td>
<td>4744</td>
</tr>
<tr>
<td>Hafnium (Hf)</td>
<td>13.3</td>
<td>178.5</td>
<td>2233</td>
<td>4603</td>
</tr>
<tr>
<td>Vanadium (V)</td>
<td>6.90</td>
<td>50.9</td>
<td>1910</td>
<td>3407</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>7.15</td>
<td>52.0</td>
<td>1907</td>
<td>2671</td>
</tr>
<tr>
<td>Zirconium (Zr)</td>
<td>6.52</td>
<td>91.2</td>
<td>1855</td>
<td>4409</td>
</tr>
<tr>
<td>Titanium (Ti)</td>
<td>4.51</td>
<td>47.9</td>
<td>1668</td>
<td>3287</td>
</tr>
</tbody>
</table>

Source: (Lide 2007)
To meet the design goals of future rocket motors, materials exhibiting high strengths and resistance to erosion are required. Tungsten, as well as similar refractory metals such as molybdenum (Mo), tantalum (Ta), hafnium (Hf), and rhenium (Re), have been identified as potential materials for future rocket nozzles (Kuo et al. 2005). Performance evaluation of these materials using subscale test firings of rockets could be used; however, these tests require significant time and money, particularly at the high pressures and temperatures of future systems. The uses of analytical and numerical models are therefore desired. In order to model such phenomena as accurately as possible, the development of simple and concise homogeneous and heterogeneous reaction mechanisms for high temperature tungsten oxidation are required to make appropriate predictions of nozzle erosion rates. A better understanding of tungsten-based nozzle corrosion processes would also aid scientists and engineers in developing new rocket propellants and nozzle throat erosion mitigation strategies. Future propellant formulations could be tailored to produce combustion products that minimize the nozzle erosion rates. Similarly, it has been demonstrated that controlling gas-phase composition within the boundary layer of the nozzle can lead to significantly reduced nozzle erosion rates (Acharya and Kuo 2007b; Evans et al. 2009). Improved understanding of the chemical reactions involved may lead to further erosion mitigation.

The thermal and chemical requirements of rocket motor nozzles apply to other aerospace components as well. In high-speed flight or re-entry vehicles, aerodynamic heating causes excessive temperatures, particularly at leading edges or areas of fluid stagnation (Sherman 1978). For instance, an object traveling at Mach 1 in still 0°C (273 K) air produces a leading edge or stagnation temperature of approximately 330 K, according to isentropic compressible flow relations (Kueth and Chow 1986). Likewise, at Mach 2, 490 K; Mach 5, 1640 K; and Mach 10, 5700 K. Obviously in some aerospace applications materials such as tungsten may be needed to deal with the high temperatures associated with aerodynamic heating. The availability of detailed high temperature reaction mechanisms greatly eases evaluation of tungsten as an appropriate material.

Another field in which high temperature heterogeneous reaction mechanisms for tungsten may be beneficial is in fusion reactors, proton accelerators, or plasma targets. Tungsten is currently being employed as a first wall material in fusion reactor designs. The high temperatures created by the plasma allow oxidation reactions to occur. Although
concentrations of oxidizing species in plasma reactors are extremely low due to a vacuum environment, even a very small amount of oxidation could reduce service lifetimes. In the case of oxidation by water vapor (Eq. 1-1), reactions could create hazardous situations due to the production of hydrogen (Smolik et al. 1998).

$$W + 3H_2O \rightarrow WO_3 + 3H_2$$  \hspace{1cm} (1-1)

In all the application areas discussed thus far, an increased understanding of the high temperature oxidation kinetics is desired in order to analyze tungsten component erosion rates or lifetimes. Tungsten oxidation has therefore been considered with negative connotations. However, in some applications high oxidation rates are desired, such as in metal particle combustion. Metallic particles, particularly aluminum, are utilized in solid propellants in order to increase energy density and performance. Particles are also used in explosives in order to increase reaction exothermicity (i.e., temperatures) and reaction rates. Many metals are seeing renewed interest from researchers over the last decade as material processing technology has progressed, allowing for the production of particles with nanometer dimensions. As particles are decreased in size, increasing the surface area to volume ratio, many interesting properties are found relating to combustion. Nanoscale metal (fuel) particles offer several significant advantages including reduced melting temperatures, combustion times, ignition temperatures and delays (Mench 1998; Risha et al. 2002; Risha et al. 2008; Sabourin et al. 2008; Sabourin et al. 2009). Tungsten is a material of interest to combustion scientists and engineers since it exhibits a highly exothermic reaction, like many metals, and because of its high density, theoretically providing high combustion heat releases per unit volume (Table 1-2). Tungsten is currently used in many weapons systems as a high density penetrator in munitions and warheads, and has been studied sparingly as an additive in particle form (Ivanov et al. 1982; Goldstein and Mader 1985; Kato et al. 2006). The development of a predictive oxidation reaction mechanism provides a tool for predicting performance of these mixtures, as well as designing munitions and reactive materials that utilize the high density and reaction properties of tungsten.
Recent studies have been directed toward the synthesis of nanoscale tungsten oxides from tungsten substrates (Xu et al. 2006; Xu and Tse 2007; Zhang et al. 2008). These oxides have generated interest in regards to their applications in optics, chromatic sensors, and catalysis. The availability of a tungsten oxidation mechanism would greatly increase the development and understanding of these synthesis processes.

Although several applications are presented for the utilization of a detailed tungsten oxidation mechanism and predictive empirical correlations, the primary focus of this work is solving problems related to tungsten rocket nozzle erosion. Therefore, the oxidation conditions found in rocket motors are most often considered and therefore discussed in detail.

### 1.2 Research Objectives

The overall goal of this research is to enhance the current understanding of high temperature tungsten oxidation, and refine methods for developing heterogeneous reaction kinetics. In order to achieve these goals, the major objectives of this investigation were to:

- Develop experimental techniques for measuring kinetically limited oxidation rates of bulk tungsten.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Oxide Product</th>
<th>$MW$, g/mol (metal)</th>
<th>$\rho$, g/cm$^3$ (metal)</th>
<th>$Q$, kcal/gm of metal</th>
<th>$Q$, kcal/cm$^3$ of metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron ($B$)</td>
<td>$B_2O_3$</td>
<td>10.82</td>
<td>2.50</td>
<td>14.05</td>
<td>35.12</td>
</tr>
<tr>
<td>Titanium ($Ti$)</td>
<td>$TiO_2$</td>
<td>47.90</td>
<td>4.50</td>
<td>4.714</td>
<td>21.21</td>
</tr>
<tr>
<td>Tungsten ($W$)</td>
<td>$WO_3$</td>
<td>183.86</td>
<td>19.3</td>
<td>1.096</td>
<td>21.15</td>
</tr>
<tr>
<td>Aluminum ($Al$)</td>
<td>$Al_2O_3$</td>
<td>26.98</td>
<td>2.70</td>
<td>7.422</td>
<td>20.04</td>
</tr>
<tr>
<td>Silicon ($Si$)</td>
<td>$SiO_2$</td>
<td>28.09</td>
<td>2.49</td>
<td>7.750</td>
<td>19.30</td>
</tr>
<tr>
<td>Molybdenum ($Mo$)</td>
<td>$MoO_3$</td>
<td>95.95</td>
<td>9.01</td>
<td>1.856</td>
<td>16.72</td>
</tr>
<tr>
<td>Tungsten ($W$)</td>
<td>$WO_2$</td>
<td>183.86</td>
<td>19.3</td>
<td>0.767</td>
<td>14.79</td>
</tr>
<tr>
<td>Iron ($Fe$)</td>
<td>$Fe_2O_3$</td>
<td>55.85</td>
<td>7.86</td>
<td>1.764</td>
<td>13.86</td>
</tr>
<tr>
<td>Zinc ($Zn$)</td>
<td>$ZnO$</td>
<td>65.38</td>
<td>7.14</td>
<td>2.135</td>
<td>12.13</td>
</tr>
<tr>
<td>Nickel ($Ni$)</td>
<td>$NiO$</td>
<td>58.69</td>
<td>8.90</td>
<td>0.976</td>
<td>8.688</td>
</tr>
<tr>
<td>Copper ($Cu$)</td>
<td>$CuO$</td>
<td>63.54</td>
<td>8.93</td>
<td>0.587</td>
<td>5.244</td>
</tr>
</tbody>
</table>

Source: (Fischer and Grubelich 1998)
• Experimentally quantify high temperature kinetics of tungsten involving single and multi-component oxidizers of interest in energy and combustion systems.

• Experimentally determine the effects of multi-component gas-phase mixtures in energy and combustion systems on tungsten oxidation processes. Mixtures may be composed of multiple oxidizing species or a single oxidizing species with one or more non-oxidizing species.

• Numerically model experimental conditions so that simplified kinetic mechanisms may be developed, which can be easily implemented into more advanced models.

• Develop an initial comprehensive heterogeneous tungsten oxidation reaction mechanism with associated global kinetics for common gas-phase oxidizers.

• Identify areas for future experimental research, and identify important processes requiring detailed molecular modeling.

1.3 Outline of Dissertation

This dissertation presents background information on high temperature oxidation of tungsten, as well as experimental investigations of oxidation by gases present in many energy systems. These experimental results are used for comparison with previous results, as well as baseline results for the development of heterogeneous reaction mechanisms. The mechanisms were developed using a numerical model of the flow reactor from which global oxidation kinetics were also obtained. The outcome of this work may be used in cooperation with gas-phase mechanisms to model and predict tungsten oxidation rates at high temperatures, as well as an outline for developing new heterogeneous reaction mechanisms in the future.

Chapter 2 presents a background and review of metal oxidation, tungsten and its properties, as well as a review of previous literature on gas-tungsten surface interactions and oxidation kinetics. Additionally, intermediate and product oxidation species are discussed. As the primary application for this work, an introduction to rocket nozzle erosion is also presented, and previous studies of tungsten-based nozzle erosion are reviewed.
Chapter 3 describes the experimental setup used for the analysis of high temperature oxidation rates. This included sample preparation, testing procedures, as well as system monitoring and control. Test validations are discussed in detail, as well as methods of analyzing experimental data.

Chapter 4 presents the theoretical approach taken in order to predict relevant species involved in high temperature and pressure tungsten oxidation, as well as the respective elementary reaction steps and associated kinetics. The numerical model of the flow reactor used to determine oxidation kinetics is also presented along with the relevant assumptions and governing equations (FORTRAN code provided in Appendix D). The gas-phase reaction mechanisms are presented, which were not developed as part of this dissertation, in addition to validations of the flow reactor model’s accuracy, and theoretical approaches taken to develop thermodynamic and kinetic aspects of surface species.

Chapter 5 delivers the experimental results found using the flow reactor. Three oxidizing species are evaluated in detail, oxygen ($O_2$), carbon dioxide ($CO_2$) and water ($H_2O$). Effects of non-oxidizing species – carbon monoxide ($CO$), nitrogen ($N_2$), hydrogen ($H_2$) – are also explored. Included in this chapter is the relevance of these results to rocket nozzle erosion. New and interesting perspectives of this problem are discussed. Appendix A presents similar studies using bulk graphite, another commonly used rocket nozzle material. The high temperature reactions in non-oxidizing and oxidizing atmospheres are evaluated and analyzed, producing important kinetic and phenomenological details of graphite corrosion.

Chapter 6 follows with a presentation of theoretical modeling and mechanism development processes using the thermodynamic calculations and the numerical flow reactor model. A mechanism for tungsten and $O_2$ reaction, developed using the numerical model, and evaluated using experimental data from this study, is supplied. Initial steps taken for developing more advance mechanisms involving $CO$, $CO_2$, $H_2$, and $H_2O$ species is also presented. Detailed discussions and presentations of the thermodynamic calculations are given in Appendix B.

Chapters 7 and 8 conclude this dissertation with a summary of this work, including prominent conclusions. Chapter 8 provides recommendations for future experimental and
theoretical work involving the topics of heterogeneous mechanism development and nozzle erosion mitigation strategies.

Two additional appendices are also provided at the end of this dissertation. Appendix C presents an introduction and analysis of diffusion limited heterogeneous reactions. Comparisons are drawn with the experimental data from this study. Appendix D provides the numerical model’s FORTRAN code for future reference.
Chapter 2
BACKGROUND AND REVIEW

A great deal of work has been devoted to understanding tungsten oxidation reactions in high temperature, low pressure environments. Results of these studies have led to a good phenomenological understanding of the bulk (i.e., macroscopic) oxidation processes and some understanding of kinetics. These studies have helped mitigate the corrosion of pure tungsten or tungsten-based alloys, but much is still to be learned. There has been very little work devoted to understanding high temperature (>1000°C) oxidation kinetics from a molecular or mechanistic level. Even less has been devoted towards understanding the oxidation mechanisms in high pressure environments (≥ 1 atm), as is generally the case in many energy systems, where high temperature materials are required to maximize chemical efficiencies and energy densities. The following chapter introduces the properties of tungsten, reviews our phenomenological and chemical kinetic understanding of tungsten oxidation processes, and discusses their role in rocket nozzle erosion.

2.1 High Temperature Metal Oxidation

Metal oxidation, described in the simplest of terms, is the conversion of a metal into another compound through reaction between the metal and some substance in its environment (Brown et al. 1997). When metals undergo oxidation they lose electrons – forming cations and oxidizing the metal. This process of losing electrons is termed oxidation, since the first studies of this process involved oxygen, and indeed most metal oxidation reactions involve oxygen in some form. An example of an oxidation process involving tungsten is illustrated in Eq. 2-1. Generally, this process will form its most common oxidation state, tungsten trioxide (\(WO_3\), oxidation state or number of +6), which is yellow in its solid form. In this reaction, as well as other metal oxidation reactions, the oxidizing species is reduced (i.e., gains electrons), forming a chemically bound metal oxide. These reactions are often termed oxidation-reduction reactions, or redox reactions. Although
metal oxidation reactions may seem simple, it is actually very complex at the molecular level in terms of the reaction path or mechanism (i.e., transfer of chemical bonds), and depends on a variety of factors (e.g., temperature, pressure, oxidizing mixture constituents, surface conditions, etc.).

\[ xW(b) + \frac{1}{2} yO_2(g) \rightarrow W_xO_y(b) \]  

(2-1)

When writing detailed reaction mechanisms of heterogeneous processes such as metal oxidation, several formalisms may be used. One commonly used software package for describing heterogeneous chemical kinetics, SURFACE CHEMKIN, has established a flexible and detailed formalism (Coltrin et al. 1991). In this formalism, reaction species are separated into three broad classifications or types: gas-phase (g), surface (s), and bulk-phase (b). Often the gas-phase subscript is omitted. Using this convention, the number of surface sites must be conserved. For instance, if a gas-phase molecule, \( X \), which may be annotated by \( X(g) \), is adsorbed onto a surface species, \( Y(s) \), the adsorption reaction is described as Eq. 2-2. In this manner, the top most species layer is always designated as a surface species. Likewise, if a surface species desorbs from the surface, the next lower bulk species becomes a surface species.

\[ X(g) + Y(s) \Leftrightarrow X(s) + Y(b) \]  

(2-2)

As with all gas-solid heterogeneous reactions, metal oxidation reactions are coupled to molecular gas-phase transport (see Fig. 2-1). Before any surface reactions may occur, a gas-phase species must reach the surface by convection or diffusion and adsorb onto the surface. After adsorption of a gas-phase species, reactions may occur with another adsorbed species, gas-phase molecules, or with the metal substrate. In many systems, adsorbed molecules may migrate across the metal surface, leading to subsequent reaction or desorption. When the metal is oxidized by an adsorbed oxidizing species, three different scenarios may occur. These oxidation processes are shown schematically in Fig. 2-2. If a solid or liquid oxide is formed, a diffusion barrier is created between the gas-phase oxidizer and the metal substrate. Subsequent oxidation is limited until the condensed-phase oxide layer is removed due to various mechanisms. In the case of high temperature tungsten oxidation, as well as many other refractory metal systems, vapor-phase oxides are most often
formed and transported away from the surface. In very fast reactions, production of vapor-phase oxides or reaction bi-products lead to a surface “fuming” or “blowing” effect that can affect reaction rates, particularly in diffusion limited systems. Diffusion limited oxidation is found in many reaction systems, particularly reactions involving very high temperatures such as combustion. In a kinetically limited reaction the rate of chemical reaction (i.e., bonding and dissociation) limit rates, whereas diffusion limited reactions are restricted by the diffusion or transport of reactants – metal and oxidizer – to or away from each other. The diffusive rates are a function of several variables, including temperature, and mixture concentrations. These effects should be considered when designing and interpreting experimental analyses of high temperature oxidation kinetics. Further details of diffusion limited heterogeneous reactions may be found in Appendix C.

Figure 2-1: Schematic of the coupling processes between gas-phase species and heterogeneous surface reactions, adapted from: (Kee et al. 2003).
In certain systems, two or three different oxide phases can form simultaneously, depending on the thermodynamics and reaction kinetics. Given that this survey involves vapor-phase oxide formation, for further information regarding the mechanisms and models of condensed-phase oxide formation, the reader is referred to two of many available sources (Kofstad 1988; Birks et al. 2006).

Adsorption has been widely studied for decades, and is comparatively well known weighed up against other steps in the oxidation process. There are thousands of papers and textbooks discussing adsorption due to its importance in all heterogeneous processes. When adsorption takes place, Gibbs free energy is decreased. In fact, adsorbed states are typically more stable than the most stable compound of the same gas-phase state (Kofstad 1988). Additionally, since the adsorption process reduces the translational freedom of motion of gas molecules, entropy is decreased. Using the definition of Gibbs energy (Eq. 2-3), it is shown that most gas-solid adsorption processes are exothermic – the change in enthalpy ($\Delta H$) is less than zero – due to the simultaneous decrease in free energy and entropy.

Figure 2-2: Reaction progressions of high temperature metal oxidation.
Adsorption processes are generally classified in terms of heat of adsorption (i.e., the bonding strength between the adsorbed species and the metal surface) and placed into two categories, physical and chemical. In physical adsorption (i.e., physisorption) there are no direct chemical bonds formed, no significant changes in electronic structure, and it is believed that the molecules attach to the surface by van der Waals forces. Physical adsorption is sometimes called van der Waals adsorption because of this. A molecule is chemically adsorbed (i.e., chemisorbed) if there is a significant perturbation of its electronic structure and a chemical bond is formed. Although there is no firm quantitative rules for determining the difference between the two types of adsorption, typical heats of adsorption have orders of magnitude of 15 – 100 kcal/mol (62.8 – 419 kJ/mol) and 2 – 10 kcal/mol (8.4 – 41.9 kJ/mol) for chemical and physical adsorption, respectively (Masel 1996). Due to the high reactivity between metals and oxidizing species, chemisorption primarily occurs at metal surfaces. This is true with non-oxidative species as well, such as $H_2$. Since a chemical bond is formed during the chemisorption process, there is an associated activation or energy barrier that may slow the adsorption process, whereas physical adsorption proceeds without the need to overcome an activation barrier; essentially physisorption may occur as fast as molecules collide with the surface. However, in many cases involving molecular adsorption onto metal surfaces, activation energies are so small that chemical adsorption on clean surfaces occur at the rate of collision. The thermochemical differences in these processes are shown in Fig. 2-3. The required activation energy is represented by $E$, while the heats of adsorption are represented as $\Delta H_i$. The diagram shows that the chemisorption process produces a greater degree of intimacy between the surface and the adsorbate than with physisorption. This figure helps illustrate how surface species’ thermodynamic quantities such as heat of formation may be estimated. Unlike solid and gas-phase species, little is known about the energetics of many surface complexes. By determining the heat (i.e., enthalpies) of adsorption (or desorption), which may be done using several experimental and theoretical techniques, the enthalpy of formation of the surface species, $Z(s)$, may be estimated if the gas-phase ($Y(g)$) and metal surface ($X(s)$) quantities are known (see Eq. 2-4). Some uncertainty is constantly present in this estimation due to errors in the estimated heat of adsorption processes are generally classified in terms of heat of adsorption (i.e., the bonding strength between the adsorbed species and the metal surface) and placed into two categories, physical and chemical. 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adsorption ($\Delta H_c$) value and enthalpy of formation of the clean metal surface. Most often the clean metal surface value is considered equal to that of the bulk material or slightly higher, since surface atoms are less stable than bulk atoms due to a lower coordination with adjacent atoms.

In addition to the two classifications of adsorption based on the surface bonding, adsorption processes may be differentiated even further. Non-dissociative adsorption, sometimes called molecular adsorption, occurs when the adsorbate molecule stays intact, whereas dissociative adsorption causes the molecule to dissociate. Generally, metal surfaces favor dissociative adsorption of molecules, particularly at higher temperatures. Often molecules will dissociate upon adsorption, even on low temperature metal surfaces. The chemical bonds of gas-phase molecules are often more easily broken at surfaces, as opposed to homogeneously, which leads to increased reaction rates, a result that is often exploited in heterogeneous catalytic processes.

The adsorption of molecules onto any surface is often affected by the surface structure or morphology. The term “active site” is used to describe a special site that is either required or preferred for adsorption and reaction (Masel 2001). Ideally, metal surface atoms

![Figure 2-3: Potential energy curves of physical (curve I) and chemical (curve II) adsorption processes, source: (Glassstone et al. 1941).](image)

\[
H_{f',Z_{(s)}} = \left( H_{f',X_{(s)}} + H_{f',Y_{(g)}} \right) + \Delta H_c
\]  

(2-4)
may be considered as a smooth flat surface. In actuality, surfaces may be made up of several crystallographic planes with varying atomic densities. Often chemisorption is a function of the crystallographic face orientation, as well the number of ledges, kinks, or other variations or defects in surface structure (see Fig. 2-4). These defect sites often have a lower coordination with adjacent atoms than sites within the crystallographic plane. This makes these sites better candidates for adsorption and reaction. The irregularity of the surfaces at the atomic level creates variations in the surface reaction site activity. Newer surface microscopy techniques, such as scanning-tunneling microscopy (STM), have illustrated this phenomena in great detail (Zambelli et al. 1996). Although surface structure sensitive reactions are prevalent, this in no way dictates that reactions must, or will occur at an active site. Further complicating adsorption processes are the effect of adsorbate-adsorbate interactions. The interplay between molecules affects the chemical bonding and thermodynamics, creating heats of adsorption that are surface coverage dependent (Chen et al. 2007).

The steps of the oxidation process after molecular adsorption are much less understood due to the lack of tools available for studying such processes. High temperatures lead to fast reactions, and bulk material interactions with the adsorbed species make the measurement of reaction intermediates extremely difficult. In fact, much of the vast information in regards to adsorption has been gathered at temperatures lower than those of the primary focus for this study. Many conclusions regarding the oxidation process must be extrapolated from results obtained at lower temperatures. Less is understood about high

![Figure 2-4: Schematic of a metal surface with different types of surface structures, source: (Houston 2006).](image)
pressure (i.e., > 1 atm) reactions. Experimental techniques of measuring metal oxidation, both from a global and elemental perspective, are extremely limited at high pressure. Most fundamental studies of elemental steps such as molecular adsorption are completed under vacuum, creating a great disparity between experimental and application pressures. Understanding of this disconnect in pressures is incomplete, and therefore will provide research activities for scientists and engineers for years to come.

Three theories are used to describe reactions occurring at surfaces, two of which involve an extraordinary chemist and physicist named Irving Langmuir (1881 – 1957). These reaction mechanisms are often used to describe surface catalyzed reactions; however, they may be applied to metal oxidation as well. The Langmuir-Hinshelwood mechanism (‘a’) describes reactions occurring on a surface between two fixed adsorbed species, as shown in Fig. 2-5. Species $A$ and $B$ represent the adsorbed molecules, which may be identical or different species in the case of metal oxidation. The second mechanism is not as common as Langmuir-Hinshelwood. The Langmuir-Rideal (‘b’), also called the Rideal-Eley, mechanism postulates that only one of the gas-phase reactants needs to adsorb onto the surface, and a second gas-phase species reacts directly with the adsorbed species. A third mechanism involves species $A$ and $B$ finding each other through surface migration, leading to subsequent reaction (‘c’, precursor mechanism).

Desorption processes are understood better than reaction and migration of surface species, and are likely rate-controlling steps in many reaction mechanisms since high activation energies are often associated with desorption. As opposed to adsorption, which is usually exothermic in nature, desorption processes are usually endothermic. Low pressure, high temperature desorption species may be measured using mass spectroscopic techniques.
This information provides an endpoint for the surface reaction process, allowing for interpretation of reaction mechanisms.

Although experiments are often limited to environments that do not represent application conditions, an advantage of studying high temperature metal oxidation is that often quasi-equilibrium reaction conditions may be assumed. This implies that the reactions are fast enough at high temperatures that chemical equilibrium is obtained adjacent to the metal surface. This allows for the vast array of information regarding individual species thermodynamics to be used to predict reaction products, which provide an indication of possible intermediates and desorption species. Additionally, the effects of pressure on reaction thermodynamics are well understood, allowing equilibrium calculations to provide a tool for narrowing the gap between different temperature and pressure conditions.

Most heterogeneous oxidation reactions, like the majority of exothermic reactions, may be described using the Arrhenius rate law (Eq. 2-5). This equation expresses the temperature dependence of the rate constant $k$, where $Ea$ is the apparent activation energy or heat of activation, $A$ is the pre-exponential or frequency factor, and $Ru$ is the universal gas constant. If metal oxidation of the type shown in Eq. 2-6 is studied, the pressure (i.e., oxidizer concentration) and temperature dependent chemisorption rates may be depicted by Eq. 2-7, where $P_{oxidizer}$ is the partial pressure of the oxidizing species and $n$ is the pressure dependence, which usually varies between 0.5 – 1.0 (Hastie 1975). The term $1 – \theta$ represents the fraction of metal surface sites available for adsorption and consequential reactions (i.e., $\theta$ is fraction of active surface sites covered by molecules). In cases which $n = 1$, rates are proportional to the collision rate of oxidizing species, whereas when $n < 1$, rates are limited by surface dissociation and/or subsequent reactions occurring on the metal surface. The desorption rate is proportional to $\theta$ as well (Eq. 2-8).

$$k = A \cdot \exp\left(\frac{-Ea}{Ru \cdot T}\right)$$  \hspace{1cm} (2-5)

$$\text{solid metal} + \text{gas oxidizer} \xrightleftharpoons{\text{adsorption}} \to \text{surface oxide} \xrightarrow{\text{desorption}} \text{oxide vapor} \hspace{1cm} (2-6)$$

$$\text{adsorption rate} = k_a (1 - \theta)(P_{oxidizer})^n \hspace{1cm} (2-7)$$
desorption rate \( = k_d \cdot \theta \) \hfill (2-8)

From the standpoint of the Arrhenius equation, the two most important factors needed to describe the rate of an oxidation reaction are the frequency factor and activation energy. This applies to both the global reaction, as well as elementary reaction steps. The activation energy for a reaction may be estimated theoretically with the use of quantum mechanics, while the frequency factor may be estimated using collision theory, statistical mechanics, or other forms of kinetic theory. For further information regarding the theory and procedures of these determinations the reader is referred to several sources (Glassstone et al. 1941; Laidler 1965; Kee et al. 2003; Houston 2006).

### 2.1.1 Experimental Methods for Kinetics Measurement

There are several experimental methods for measuring the oxidation rate of metals at high temperature. All of these methods measure the global reaction rate of the metal, and are not able to measure individual reaction steps. These methods either measure changes in sample mass or dimensions, or they measure changes in reactant volume or concentration.

Gravimetric methods of measuring high temperature oxidation, termed thermogravimetry, are the most prevalent and several companies make commercial thermogravimetric (TG) analysis equipment. Prior to the availability of precision recording balances, changes in sample mass were measured before and after testing, or were recorded manually by measuring changes in deflection of a high sensitivity spring or beam. New balances simultaneously measure and record mass changes as a function of time, greatly improving accuracy and uncertainty in measurements. In systems that produce condensed phase products, a mass gain is produced; initial rates are generally fast, and then diminish as oxide layer thickness is increased. In systems that produce vapor-phase oxides, a continuous mass loss is found; at constant temperature and pressure, the rate of sample mass loss is linear for a constant surface area sample.

Other methods are less often used due to inherent limitations in their measurement. Thermogravimetric measurements can assess systems involving mass loss and gain equally
as well, while measuring changes in surface dimensions due to oxidation are generally limited to mass loss systems. Although oxidation of solid metals such as iron or aluminum produce a change in sample dimension due to solid oxide formation, this may not be used to make conclusions regarding the extent of reaction since the condensed phase density profile is unknown. In the case of high temperature oxidation of tungsten and other refractory materials, where oxides may vaporize as they are formed, the condensed phase density may be assumed constant throughout the sample, therefore the change in material dimensions may be directly related to the reaction rate. Another drawback of this method is the difficulty in measuring the changes in dimensions accurately during testing, which often relegates researchers to measure pre- and post-test dimensions, increasing uncertainty of measurements.

Volumetric or manometric methods, which were often used in early experiments of high temperature corrosion, are capable of measuring reaction rates of mass gain and loss systems. These methods are also termed gas consumption methods, since they measure the change in reactant pressure or volume as a function of time. In a constant volume system, the pressure is directly proportional to the reaction rate, and therefore it is measured continuously. In a constant pressure system, the change in volume is measured continuously. The problem with the former system is that the reactant concentration (i.e., oxidizer partial pressure) is continuously changing, which directly affects oxidation rates. In both systems, the temperature and pressure must be monitored and controlled precisely to decrease uncertainties in measurement. Additionally, testing using these methods is often limited to low pressures and pure gas atmospheres to limit uncertainty.

Heating the metal samples in a controlled manner may be done in several ways. The sample may be heated directly by applying an electrical current, which heats the sample by Joule heating. This method is generally reserved for small diameter samples that demonstrate high resistance. Joule heating may be applied to specifically designed heating elements such as nichrome (nickel-chromium mixture), silicon carbide (SiC), or molybdenum disilicide (MoSi2), which can be used to heat a sample in a furnace or oven configuration by both radiation and convection. Other more elaborate mechanisms of heating metals are through pure radiant or induction heating. Radiation heating of large samples to extremely high temperatures requires the use of an infrared (IR) laser (e.g., CO2 laser), which can be
expensive and introduce several variables, making precise control of sample temperature
difficult. Small samples may be radiatively heated using other sources as well, particularly in
vacuum environments. Since many metals have low emissivities and high reflectivity, high
power radiant sources may be required to reach desired temperatures. In the case of CO$_2$
laser heating, IR reflections can lead to hazardous situations.

Induction heating uses a high frequency alternating current (AC) generator to induce
eddy currents within an electrically conducting sample. Electrical resistance of the sample
creates the Joule heating effect, and sample temperatures may be controlled by adjusting
frequency and power of the AC generator. Induction heating has several advantages and
disadvantages. Samples are limited to materials that are electrically conductive, and often
very large AC generators are required to meet design goals, making systems more expensive
than more widely used furnaces. Induction heating allows samples to be heated rapidly to
extreme temperatures in environmental containers or flow reactor tubes made of non-
conductive materials, making them a strong candidate for extremely high temperature TG
applications, or in situations where it may be desired to alter system pressures. Unlike
traditionally used furnaces, when using radiant or inductive heating the gases in the
environment may not be raised to the same temperature as the metal sample, which may be
beneficial if studying gas-phase reactants that dissociate or react easily with other gas-phase
species at high temperatures.

2.1.2 Heterogeneous Reaction Mechanism Development

Unlike homogenous reactions, there is much that is unknown about the reaction
mechanisms of heterogeneous chemical processes. Additionally, approaches for developing
a reaction mechanism are significantly lacking relative to gas-phase mechanisms, both in
terms of developmental efficiency, standardization, and tools. Figure 2-6 illustrates the basic
process for the development of a heterogeneous reaction mechanism. All researchers
developing a heterogeneous reaction mechanism should use this procedure, although tools
may change depending on the reaction system and resources available. The order in which
some of these steps are undertaken may be altered, and many steps may be accomplished in
parallel, however, all steps must be taken. This approach is a modification of a standardized
approach for developing homogeneous reaction mechanism (Westbrook and Dryer 1981; Yetter et al. 1995).

Figure 2-6: Approach to heterogeneous reaction mechanism development.
2.2 Tungsten

Tungsten is a very hard and heavy refractory material with the chemical symbol \( W \) (German: wolfram). It is a metallic grey transition metal that has the highest melting point and tensile strength, and lowest vapor pressure of all pure metals. Only carbon has a higher melting point of all the elements. Due to these properties, tungsten is used in several unique applications, outlined below (Lassner and Schubert 1999):

- Coils, filaments, or electrodes for lamps
- Electrical contacts in high performance systems
- High temperature furnace heating elements and radiation shields
- High temperature thermocouples
- High performance alloys used in high speed machining, or other high temperature and abrasive environments
- Construction parts for nuclear and fusion reactors
- High temperature propulsion equipment
  - Combustion chambers
  - Ignition tubes
  - Rocket motor nozzles
- Space and aviation equipment
- Electrodes for welding, electrical discharge machining (EDM), arc and wire erosion
- Vapor deposition material
- Anodes and cathodes in X-ray tubes
- X-ray shielding
- Electron emitters for high resolution spectroscopic imaging (SEM, FE-SEM, etc.)
- Sporting goods (used where inert, high density materials are desired)
- Kinetic energy penetrators for ammunition (Cho et al. 2007)

The various physical and thermochemical properties of tungsten, which is a body centered cubic (BCC, 316 pm cell dimension) metal, are presented in Table 2-1, as well as in Table 1-1.
2.2.1 Reactions and Compounds

Although tungsten is best known and lauded for its physical properties, the chemical properties and reactions involving tungsten limit its applications. In contrast to tungsten’s hard, dense, and strong character, it is very susceptible to reactions at elevated temperatures; in fine powdered form it is a combustible substance.

In many cases, tungsten performs well and is considered inert up to very high temperatures. It is relatively unreactive with many ceramics, glasses, molten metals, and mineral acids. However, it may be vigorously attacked by oxidative compounds such as oxygen or fluorine. Table 2-2 presents basic reactions of nonmetal elements with tungsten. Although tungsten reacts with many nonmetals, notable exceptions include hydrogen and nitrogen. Molecular nitrogen does not react directly due to its high bond strength, unless

Table 2-1: Select properties of solid-phase pure tungsten.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Number</td>
<td>74</td>
</tr>
<tr>
<td>Atomic Volume</td>
<td>9.53</td>
</tr>
<tr>
<td>Specific Heat, Cp</td>
<td>24.295 @ 298.15 K</td>
</tr>
<tr>
<td></td>
<td>27.564 @ 1000 K</td>
</tr>
<tr>
<td></td>
<td>32.254 @ 2000 K</td>
</tr>
<tr>
<td></td>
<td>41.003 @ 3000 K</td>
</tr>
<tr>
<td>Heat of Fusion</td>
<td>35.4</td>
</tr>
<tr>
<td>Heat of Vaporization</td>
<td>799</td>
</tr>
<tr>
<td>Coefficient of Linear Thermal Expansion</td>
<td>4.6</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>10.133 @ 3820 K</td>
</tr>
<tr>
<td></td>
<td>101.33 @ 4210 K</td>
</tr>
<tr>
<td></td>
<td>1013.3 @ 4710 K</td>
</tr>
<tr>
<td></td>
<td>10133 @ 5350 K</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>186 @ 200 K</td>
</tr>
<tr>
<td></td>
<td>159 @ 400 K</td>
</tr>
<tr>
<td></td>
<td>118 @ 1000 K</td>
</tr>
<tr>
<td></td>
<td>95 @ 2500 K</td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>5.65</td>
</tr>
<tr>
<td>Elastic Modulus</td>
<td>345</td>
</tr>
<tr>
<td>Young’s Modulus</td>
<td>411</td>
</tr>
<tr>
<td>Emissivity (polished W)</td>
<td>0.10 @ 1000 K</td>
</tr>
<tr>
<td></td>
<td>0.25 @ 2000 K</td>
</tr>
</tbody>
</table>

Sources: a(Lide 2007), b(Barbalace 2008), c(Chase 1998), d(ASM 1983), e(Turns and Kraige 2007)
extremely high temperature environments are involved. However, it is possible to form tungsten nitrides from ammonia or other nitrogen containing compounds at lower temperatures. Many of the elements presented in the table are not likely to be present in energy or combustion systems. The most relevant species are carbon, oxygen, and chlorine. It is important to note that although it may be stated that tungsten is non-reactive with various elements or compounds, this does not include tungsten surface bonding, which will occur with most elements and compounds.

Table 2-2: Reactions between tungsten and nonmetal elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Approximate Reaction Temperatures</th>
<th>Remarks</th>
<th>Product Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron ($B$)</td>
<td>800 – 1200°C</td>
<td>Boride formation depends on $W/B$ ratio of powder mixtures</td>
<td>$W_2B, WB, W_2B_2, WB_4$</td>
</tr>
<tr>
<td>Carbon ($C$)</td>
<td>&gt; 800°C</td>
<td>–</td>
<td>$W_2C, WC$</td>
</tr>
<tr>
<td>Silicon ($Si$)</td>
<td>Elevated</td>
<td>–</td>
<td>$WSi_2, WSi_3, W_2Si_3, W_2Si_3$</td>
</tr>
<tr>
<td>Phosphorous ($P$)</td>
<td>&gt; 700°C</td>
<td>Under vacuum</td>
<td>$WP_2$</td>
</tr>
<tr>
<td>Oxygen ($O$)</td>
<td>&gt; 400°C</td>
<td>Sublimation of oxides above ~900°C</td>
<td>$WO, WO_2, WO_3, WO_{2.27}, WO_{2.96}$</td>
</tr>
<tr>
<td>Selenium ($Se$)</td>
<td>&gt; 480°C</td>
<td>Exothermic</td>
<td>$WSe_2$</td>
</tr>
<tr>
<td>Sulfur ($S$)</td>
<td>&gt; 400°C</td>
<td>–</td>
<td>$WS_2$</td>
</tr>
<tr>
<td>Tellurium ($Te$)</td>
<td>&gt; 700°C</td>
<td>Slow reaction under vacuum</td>
<td>$WTe_2$</td>
</tr>
<tr>
<td>Fluorine ($F$)</td>
<td>Room</td>
<td>Volatile $WF_6$ primary product</td>
<td>$WF_6, WF_4, (WF_5)_4$</td>
</tr>
<tr>
<td>Chlorine ($Cl$)</td>
<td>&gt; 250°C</td>
<td>$O$ and $H_2O$ enhance attack</td>
<td>$WCl_2, WCl_4, WCl_6$</td>
</tr>
<tr>
<td>Bromine ($Br$)</td>
<td>&gt; 450°C</td>
<td>–</td>
<td>$WBr_n _2.6$</td>
</tr>
<tr>
<td>Iodine ($I$)</td>
<td>&gt; 550°C</td>
<td>$O$ and $H_2O$ enhance attack</td>
<td>$WI_2, WI_3, WI_6, WdI_{12}$</td>
</tr>
</tbody>
</table>

Adapted from: (Lassner and Schubert 1999).

Intermetallic reactions involving tungsten are not diverse. Few metals will react with tungsten and in most cases specific conditions are needed for compounds to be formed. Tungsten is soluble in many transitions metals, a property that is used to produce many specialty materials for advanced applications.

There are many compounds of all phases which will react with tungsten, most of which do in an oxidizing manner. A short summary of these reactive compounds, including oxidizing species are shown in Table 2-3.
2.2.1.1 Oxidation

At lower temperatures, tungsten oxidizes forming completely solid-phase oxides, causing a gain in mass of the base material. A TG analysis of nanoscale tungsten particles demonstrates this (Fig. 2-7). With these nanoscale particles – nominal diameter of 150 nm – reaction with oxygen is seen as low as 300°C, however, the most rapid oxidation is found at temperatures between 450 – 600°C. This temperature may change considerably depending on the tungsten substrate (i.e., morphology), oxidizer, and may be found to be a function of particle diameter below a certain value (Brandstadt et al. 2005). Vastly different oxidation profiles are found with oxygen and carbon dioxide. Although the initial oxidation process begins at approximately the same temperature with both species, the kinetics are much slower with CO₂, as would be expected given its greater thermochemical stability compared
to molecular $O_2$. Regardless of the substrate structure, preparation, and oxidizing gas, the initial oxidation rates of tungsten are found to increase exponentially with temperature, as with most other oxidation reactions. Figure 2-7 also shows a DSC (Differential Scanning Calorimetry) measurement of the tungsten oxidation process, indicating a highly exothermic reaction with $O_2$. The greater reactivity of $O_2$ compared to $CO_2$ is illustrated by a much greater total heat release in the DSC plot, as well as the data in Table 2-4. At temperatures greater than $1300^\circ C$ vaporization of the tungsten oxides begins with both oxidizing species.

![Figure 2-7: TG analysis (a) and DSC (b) of nanoscale tungsten particles in $O_2$ and $CO_2$.](image)

**Table 2-4: Tungsten heats of combustion involving various oxidizing gases.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$Q$, kcal/mol (cal/gm) of tungsten</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_{(s)} + \frac{1}{2} O_2 \rightarrow WO_{3(s)}$</td>
<td>$201.3$ ($1095$) $\rightarrow$ highly exothermic</td>
</tr>
<tr>
<td>$W_{(s)} + 3CO \rightarrow WO_{3(s)} + 3CO$</td>
<td>-1.44 (-7.83) $\rightarrow$ moderately endothermic</td>
</tr>
<tr>
<td>$W_{(s)} + 3H_2O \rightarrow WO_{3(s)} + 3H_2$</td>
<td>$28.05$ ($152.5$) $\rightarrow$ exothermic</td>
</tr>
<tr>
<td>$W_{(s)} + 3NO \rightarrow WO_{3(s)} + \frac{3}{2} N_2$</td>
<td>$266$ ($1447$) $\rightarrow$ highly exothermic</td>
</tr>
</tbody>
</table>

Diffusion limited reactions are found to occur as the oxide layer builds up. The presence of the solid oxide layer inhibited the gas-phase oxidizers from reaching the unreacted metal. Given the small dimensions of the particles studied in Fig. 2-7, transport distances of the oxidizers were small, and complete oxidation was seen. In larger bulk
materials, the transport distances become large and incomplete oxidation may be found. Studies have shown that the solid oxide layer consists of several tungsten oxides. At the surface, $WO_3$ is most likely to occur, and closer to the pure tungsten substrate, lower oxides are found (e.g., $WO_3 \rightarrow WO_{2.9} \rightarrow WO_{2.76} \rightarrow WO_2$).

Detailed reviews of tungsten oxidation are given by several sources (Barth and Rengstorff 1961; Kofstad 1966; Gulbransen 1970; Hastie 1975; Lassner and Schubert 1999). A review oxidation of $O_2$ from Gulbransen provides a simplified breakdown of the oxidation stages of tungsten, presented here in Table 2-5. The temperature ranges provided for each stage are estimated based on the work of Gulbransen, and may vary slightly from what is found by other researchers depending on experimental conditions, such as system pressure and $O_2$ partial pressure.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Reaction Conditions</th>
<th>Oxidation Phenomena</th>
<th>Rate Controlling Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$&lt; 650^\circ C$</td>
<td>Adherent oxide film or scale formed.</td>
<td>Wagner type diffusion of metal or $O_2$ through oxide.</td>
</tr>
<tr>
<td>2</td>
<td>650 – 775°C</td>
<td>Localized breakdown of oxide scale due to thermal and mechanical stresses (especially at edges).</td>
<td>Wagner type diffusion of metal or $O_2$ through oxide.</td>
</tr>
<tr>
<td>3</td>
<td>775 – 1250°C excluding very low $O_2$ pressure</td>
<td>Oxides scales formed, some oxide vaporization, lower pressures favor volatile oxides.</td>
<td>Oxide scale is not protective. Reaction may be diffusion or kinetically limited.</td>
</tr>
<tr>
<td>4</td>
<td>1250°C to the transition temperature for diffusion limiting reaction</td>
<td>No solid oxide scales formed – all volatile oxides formed.</td>
<td>Chemical or kinetically limited processes on metal or thin oxide film.</td>
</tr>
<tr>
<td>5</td>
<td>Above transition temperature</td>
<td>Formation of thick barrier or boundary layer of volatile oxides.</td>
<td>Diffusion limited. Transport of $O_2$ through barrier layer. Gas flow and concentrations are critical.</td>
</tr>
</tbody>
</table>

Source: (Gulbransen 1970).

Above approximately 1250°C no solid oxides are formed, creating a linear mass loss of the bulk tungsten material under steady-state conditions. The rate of mass loss under these conditions may be limited by reaction kinetics or diffusion of gas-phase species. The effect of gas-phase diffusion on observed reaction rates is discussed in detail in Appendix C. The temperature at which the onset of vaporization occurs has shown to be a function of atmospheric conditions as well. Additions of water vapor accelerate the vaporization process of $WO_3$ by the reaction shown in Eq. 2-9, and has shown a similar but lesser effect on lower
tungsten oxides. This reaction has been shown to cause vaporization of tungsten oxides at temperatures below 800°C (Greene and Finfrock 2001). This product species has been known for a considerable amount of time in its solid form as tungstic acid or a hydrated tungsten oxide, which is a naturally occurring compound that has long been used as a precursor in the production of pure tungsten.

\[
WO_3(\text{liq. or solid}) + H_2O(g) \rightarrow WO_3 \cdot H_2O(g) \text{ or } WO_2(OH)_{2(g)} \quad (2-9)
\]

2.2.1.1 Literature Review of Oxidation Studies

In order to model and understand high temperature tungsten oxidation processes, surface reaction characterization becomes a very important piece to the overall puzzle. Determination of fundamental kinetics of basic reactions involving single oxidizing species is the first step in building a reaction mechanism. Although heterogeneous chemical kinetics of individual species are often affected by the presence of other species, understanding individual species kinetics provide an elementary framework to build more complex models upon. To date there has been several studies of gas-solid surface reaction kinetics of bulk tungsten at high temperature, with most involving the reaction of tungsten and molecular oxygen (Baur et al. 1956; Gulbransen and Andrew 1960; Perkins and Crooks 1961; Bartlett 1964; Gulbransen et al. 1964; Walsh et al. 1967a). Less work has been done with other compounds such as carbon dioxide (Walsh et al. 1967b; Harvey 1974a), water vapor (Farber 1959; Aspinall 1965; Kilpatrick and Lott 1966; Unal et al. 2000; Greene and Finfrock 2001), atomic oxygen (Rosner and Allendorf 1967b) or nitrogen containing compounds (Farber et al. 1955). Even less has looked into how mixtures of these compounds may effect overall reaction rates (Olcott and Batchelor 1964; Rosner and Allendorf 1967a; Walsh et al. 1967b; Andrievskii et al. 1981). Interesting results have been found with mixtures of gases. Hydrogen and CO have illustrated oxidation inhibiting effects, while \(O_2\) and \(Cl_2\) exhibit a synergistic effect, even though \(Cl_2\) produced little to no corrosion on its own (Rosner and Allendorf 1967a). Most of these works present a phenomenological perspective of the oxidation rates, and are inadequate in their applicability to modeling and prediction. This limited pool of available kinetic data has restricted development of new models used to
predict corrosion processes of tungsten in high temperature applications (Thakre and Yang 2009).

The investigations involving molecular oxygen are summarized in Table 2-6. The majority of the studies presented here involve conditions that produce tungsten mass loss due to the vaporization of oxide species. Global activation energies of the chemical reaction between tungsten and $O_2$ range from 14.3 to 48 kcal/mol, though the most agreeable studies indicate an activation energy of the order of 23 – 33 kcal/mol. All researchers found a net loss of tungsten due to oxide vaporization at temperatures greater than or equal to 1300°C. Each study provides a good qualitative understanding of the oxidation process. However, many suffer from diffusion limited reactions at high temperatures, skewing kinetic results, or do not present correlations or detailed mechanisms for the oxidation reaction.

An early correlation for tungsten oxidation kinetics was developed by Ong using data from previous researchers (Baur et al. 1956; Webb et al. 1956; Gulbransen and Andrew 1960; Ong 1962), as well as chemical kinetics and gas diffusion theories (Eq. 2-10). The correlation developed by Ong was stated to be valid at temperatures greater than 700°C, where the pressure is in atm.

$$
\dot{W}_{\text{O}_2}^{\text{Ong}} = 8.9 \times 10^{-3} \frac{\text{moles of } W}{\text{cm}^2 \cdot \text{s} \cdot \text{atm}^{0.5}} \exp \left( \frac{-24.2 \text{kcal/mol}}{R \cdot T} \right) \cdot \left( P_{\text{O}_2} \right)^{0.5}
$$

(2-10)

The works from Gulbransen et al. have provided a thorough overview of the tungsten and oxygen reaction process as a function of temperature (Gulbransen and Andrew 1960; Gulbransen et al. 1964; Gulbransen 1965; Gulbransen 1970). These publications discuss the phases and the oxides formed, as well as limiting processes. Gulbransen et al. also presented an empirical formula for the prediction of the tungsten oxidation rate between 1350 – 1615°C, as shown in Eq. 2-11 (Gulbransen et al. 1964), where the pressure in torr. Based on earlier findings, mainly from lower temperature X-ray diffraction studies, Gulbransen surmised that the primary high temperature desorption species were $WO_3$ or its polymers. A single step reaction mechanism was presented to represent this. Unfortunately, a more detailed discussion of the reaction mechanism was not provided and the results seem to indicate the onset of diffusion limited reactions at the highest temperatures studied.
Table 2-6: Summary of experimental high temperature $W-O_2$ oxidation kinetics studies.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(Baur et al. 1956)</td>
<td>(assumed = $P_{O_2}$)</td>
<td>1107 – 1627</td>
<td>1034 – 2584</td>
<td>TGA ($\Delta m/\Delta t$); static flow furnace</td>
<td>48</td>
<td>-</td>
<td>$WO_2$ and $WO_3$ products found</td>
</tr>
<tr>
<td>(Gulbransen and Andrew 1960)</td>
<td>$&lt;760$ (assumed = $P_{O_2}$)</td>
<td>500 – 1300</td>
<td>1 – 76</td>
<td>TGA ($\Delta m/\Delta t$); static flow furnace</td>
<td>32.5</td>
<td>-</td>
<td>Rate limited by $WO_3$ volatility, and diffusion of $O_2$ and $W_3O_9$ product; mass loss @ $T &gt; 1200ºC$</td>
</tr>
<tr>
<td>(Perkins and Crooks 1961)</td>
<td>1-40</td>
<td>1300 – 3000</td>
<td>0.21 – 8.4 (assuming 21% $O_2$ in air)</td>
<td>Surface recession ($\Delta x/\Delta t$); static flow; resistively heated sample</td>
<td>31.5 (1300 – 1750ºC)</td>
<td>0.62 (1300 – 1750ºC)</td>
<td>Above 1750ºC diffusion limited oxidation rates are found.</td>
</tr>
<tr>
<td>(Perkins et al. 1962)</td>
<td>$\sim P_{O_2}$</td>
<td>1300 – 3350</td>
<td>0.1 – 5</td>
<td>Surface recession ($\Delta x/\Delta t$); convective (turbulent) flow; resistively heated sample</td>
<td>24.5 @ high $P$; 0.83 @ high $P$; 43.9 @ low $P$</td>
<td>$WO_3$ and its polymers assumed to be the only vaporized $W$-oxides. Ong used theoretical formulations for kinetics and diffusion to develop correlation.</td>
<td></td>
</tr>
<tr>
<td>(Baur et al. 1956; Webb et al. 1956; Gulbransen and Andrew 1960)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Data from (Baur et al. 1956; Webb et al. 1956; Gulbransen and Andrew 1960) used for rate correlation</td>
<td>24.3 (T &gt; 700ºC); 0.5 (T &gt; 700ºC)</td>
<td>-</td>
<td>A transition in the reaction rate behavior occurs at high temperatures (pressure dependent). Diffusion limited reactions found at high temperatures.</td>
</tr>
<tr>
<td>(Berkowitz-Mattuck et al. 1963)</td>
<td>$\sim P_{O_2}$</td>
<td>1227 – 2527</td>
<td>$10^4 – 10^2$</td>
<td>Mass spectroscopy; radiatively heated plate</td>
<td>-</td>
<td>-</td>
<td>($WO_3h_{1/2}$ and $WO_2$ vaporized oxide species formed)</td>
</tr>
<tr>
<td>(Gulbransen et al. 1964)</td>
<td>(assumed = $P_{O_2}$)</td>
<td>1150 – 1615</td>
<td>2 – 100</td>
<td>TGA ($\Delta m/\Delta t$); static flow furnace</td>
<td>14.3</td>
<td>1.1</td>
<td>$\sim$13% of $O_2$ molecules colliding w/ surface react (i.e., sticking factor = 0.13)</td>
</tr>
<tr>
<td>(Bartlett 1964)</td>
<td>$&lt;760$ (assumed = $P_{O_2}$)</td>
<td>1320 – 3170</td>
<td>0.00076 – 760</td>
<td>Surface recession ($\Delta x/\Delta t$); resistively heated sample</td>
<td>42</td>
<td>0.55 – 0.8</td>
<td>Above 2000ºC reaction probabilities were 0.06 @ all pressures and the reaction rate was independent of T (diffusion limited); multilayer kinetic process suggested, forming $WO_2$ and $WO_3$ products</td>
</tr>
<tr>
<td>(Schissel and Trulson 1965)</td>
<td>$\sim P_{O_2}$</td>
<td>1127 – 2877</td>
<td>$\leq 2\cdot10^4$</td>
<td>Mass spectroscopy; resistively heated filament</td>
<td>-</td>
<td>-</td>
<td>($WO_3h_{1/2}$ and $WO_2$, $WO_3$ and $O$ desorption species found; 1$^{\text{st}}$ order reaction process, except for highest temperatures</td>
</tr>
<tr>
<td>(Walsh et al. 1967a)</td>
<td>2-11.1 (static)</td>
<td>1727 – 3027</td>
<td>0.11 – 11.5 (stagnation)</td>
<td>Surface recession ($\Delta (x_{\text{in}}-x_{\text{out}})/\Delta t$), high velocity jet impingement; inductively heated sample</td>
<td>23</td>
<td>-</td>
<td>Diffusion limited rates found at highest temperatures studied</td>
</tr>
<tr>
<td>(Rosner and Allendorf 1967a)</td>
<td>I</td>
<td>$\sim$1450 – 2500</td>
<td>$10^4$ ($O_2 + Cl_2$)</td>
<td>Resistance (R) change, assuming AR of resistively heated filament was proportional to area; external gas flow.</td>
<td>-</td>
<td>-</td>
<td>Chlorine ($Cl_2$) was also considered, but did not exhibit any corrosion with $W$. However, $Cl_2$ did show a significant synergistic coupling with $O_2$, enhancing corrosion rates at lower temperatures.</td>
</tr>
<tr>
<td>(Harvey 1973)</td>
<td>600</td>
<td>2177 – 2927</td>
<td>0.012 – 0.09</td>
<td>Mass change ($\Delta (m_{\text{in}}-m_{\text{out}})/\Delta t$); static flow; resistively heated sample</td>
<td>-</td>
<td>1.10 – 1.35</td>
<td>Reaction rates at constant $O_2$ partial pressure decreased w/ increasing T in this diffusion limited system</td>
</tr>
</tbody>
</table>
\[ \dot{r}_{W-O_2} \text{(Gulbransen et al.)} = 1.03 \times 10^{-5} \frac{\text{moles of } W}{\text{cm}^2 \cdot \text{s} \cdot \text{torr}^{1.1}} \cdot \exp \left( \frac{-14.3 \text{ kcal/mol}}{R \cdot \text{torr}} \right) \left( P_{O_2} \right)^{1.1} \quad (2-11) \]

The earlier work from Perkins and Crooks derived a similar expression for the \( O_2 \) pressure and temperature dependent tungsten oxidation process for temperatures between 1300 – 1750°C (Eq. 2-12) (Perkins and Crooks 1961). The parameters of the Arrhenius expression vary significantly from that of Gulbransen et al. At higher temperatures, Perkins and Crooks also determined oxidation rates to decrease with increasing temperature. At the time of this study this was not understood, however, based on the current understanding of the oxidation process, it is clear that diffusion limited reactions were measured at higher temperatures. No detailed reaction mechanisms for the oxidation process were presented by Perkins and Crooks, and as with Gulbransen et al., the oxidation product was determined to be \( WO_3 \) using thermodynamic calculations and previous studies of the oxidation system.

\[ \dot{r}_{W-O_2} \text{(Perkins & Crooks)} = 1.31 \times 10^{-3} \frac{\text{moles of } W}{\text{cm}^2 \cdot \text{sec} \cdot \text{torr}^{0.62}} \cdot \exp \left( \frac{-31.5 \text{ kcal/mol}}{R \cdot \text{torr}} \right) \left( P_{O_2} \right)^{0.62} \quad (2-12) \]

Perkins, Price, and Crooks extended the previous study over a wider range of pressures and temperatures, determining that the temperature dependence of the reaction transitions at a critical \( O_2 \) pressure (Perkins et al. 1962). The low pressure reaction rate is expressed in Eq. 2-13 below, where the transition pressure is represented by Eq. 2-14, and the higher pressure rate by Eq. 2-15. Most available data laid in the high pressure range, and in their investigation they found Eq. 2-15 to match data from Eisinger with good accuracy (Eisinger 1959).

\[ \dot{r}_{W-O_2} \text{(Perkins et al.)} = 0.216 \frac{\text{moles of } W}{\text{cm}^2 \cdot \text{sec} \cdot \text{torr}^{0.59}} \cdot \exp \left( \frac{-43.9 \text{ kcal/mol}}{R \cdot \text{torr}} \right) \left( P_{O_2} \right)^{0.59} \quad (2-13) \]

\[ P_{O_2, \text{transition}} \text{(Perkins et al.)} = 1.082 \times 10^{10} \exp \left( \frac{-93.5 \text{ kcal/mol}}{R \cdot \text{torr}} \right) \text{= Torr} \quad (2-14) \]
One of the first studies to propose a multi-step reaction mechanism was done by Bartlett (Bartlett 1964). Bartlett covered a wide range of temperatures and pressures under free convection conditions. Given the nature of the experiment used, rates above 2000°C were largely diffusion limited, which explains why temperature independent reaction rates were found. However, using mass spectroscopic (MS) studies from Berkowitz-Mattuck et al. (Berkowitz-Mattuck et al. 1963), and adsorption studies by Becker et al. and Eisinger (Eisinger 1959; Becker et al. 1961), Bartlett put forth an multilayer adsorption and reaction process (Fig. 2-8). In this model, a multilayer adsorption process was assumed, where the second layer is formed in reaction ‘b’. Desorption of vaporized species takes place in reactions ‘c’ and ‘d’. Using results of the mass spectroscopic studies, Bartlett determined that a mixture of $WO_2$ and $WO_3$ desorbs from the surface. Using simple adsorption theory, an oxygen pressure exponent of 0.5 was predicted for reaction ‘c’, while reaction ‘d’ would create an exponent of 1.0. Bartlett explained that experimentally derived exponents between 0.5 and 1.0 are an indicator that indeed $WO_2$ and $WO_3$ are both being removed from the surface. The global reaction mechanism was described as being limited by desorption of oxide species under steady state conditions.

$$
\dot{r}_{W-O_2}^{\text{Perkins et al.}} = 1.81 \times 10^{-3} \frac{\text{moles of } W}{\text{cm}^2 \cdot \text{sec} \cdot \text{torr}^{0.82}} \cdot \exp\left(\frac{-24.5 \text{ kcal/mol}}{R \cdot T}\right) \cdot P_{O_2}^{0.82} \quad (2-15)
$$

Figure 2-8: Proposed tungsten-oxygen reaction mechanism ($T < 2000^\circ C$) from (Bartlett 1964).
Shortly after these initial studies by Bartlett, another study looked at the influence of crystallographic orientation on the oxidation of tungsten (Bartlett and McCamont 1965). Three different crystal surfaces were examined: (100), (111) and (110). Results indicated that the (100) surface reacted much faster than the (111) and (110) surfaces, as would be expected from a BCC metal due to the lower coordination level of the surface atoms. The (111) face oxidized slightly faster than the (110) face, and both illustrated similar reaction rates compared to that of a polycrystalline surface.

A MS study by Berkowitz-Mattuck et al. was one of the first studies to precisely measure the vaporized oxide species formed from direct oxidation of a bare tungsten surface, as opposed to vaporization from solid oxides (Ackermann and Rauh 1963; Berkowitz-Mattuck et al. 1963). Their results showed that there were similarities between oxidation products of like metals (e.g., Mo and W), but there were distinct differences in the vaporized species of a bulk oxide surface, and a clean metal being oxidized. Before this study, most studies assumed $WO_3$ or its polymers to be the primary oxide species based on studies of the solid oxides formed. This MS study confirmed that a large amount of these species are formed, but $WO_2$ is formed in large quantities as well, particularly at the highest temperatures studied. Figure 2-9 shows the results from Berkowitz-Mattuck et al. The plots indicate that polymers of $WO_3$ are formed only at the lowest temperatures studied, and above approximately 2000 K the dominant species desorbing from the surface is $WO_2$. These results also indicated that the rate of formation of gaseous oxides during metal oxidation may not be derived purely based on thermodynamic grounds. Although species were predicted accurately using thermodynamic equilibrium calculations, concentrations differed significantly.
Another MS study was conducted by Schissel and Trulson (Schissel and Trulson 1965). This study was similar to the previous MS study, however, higher temperatures were examined and the first detailed mechanism for tungsten oxidation by $O_2$ was provided, as well as the associated kinetic parameters. Results show that at the lowest temperatures, $WO_3$ and its polymers are the primary desorption species, with $WO_2$ formation mounting in intensity with increasing temperature (Fig. 2-10). Unlike the previous study, Schissel and Trulson found some $WO$ formation at the highest temperatures. The results also indicate that at the highest temperatures, nearly all the $O_2$ molecules impinging on the surface go through a dissociative adsorption process before desorbing as $O$, $O_2$, or form a tungsten oxide.

Figure 2-9: Mass spectroscopic results for $W-O_2$ oxidation: (a) rates of oxide formation, and (b) effective interface pressure of oxides, as a function of temperature ($P_{O_2} = 7.2 \times 10^{-4}$ torr), source: (Berkowitz-Mattuck et al. 1963).
The mechanism proposed by Schissel and Trulson is provided in Table 2-7. They determined that oxygen bonds with the surface in two different sites or states, where one is bound stronger (\(WO_{(s)}\)) than the other (\(WO^*_{(s)}\)). This is similar to the multilayer process proposed by Bartlett. The reaction begins with the dissociative adsorption process of \(O_2\) onto the two types of sites. The multilayer bonding and surface sites are indicative of a surface reaction process where the dissociative oxygen bonds at two separate sites, which may be bridge (on the middle of \(W-W\) bond), on top (directly on top of \(W\)-atom), or fold sites (on top of lower layer \(W\)-atoms). The bonding of an oxygen atom on each of these types of sites will have different bond strengths and energetics. These oxygen atoms may evaporate, recombine to \(O_2\), or react with the tungsten substrate forming gas-phase \(WO_2\), or \(WO_{3(s)}\). The \(WO_{3(s)}\) species then either vaporizes or dissociates, forming \(WO_2\). The mechanism also indicates that \(WO_{3(s)}\) could combine to form vapor-phase polymers. Note that the mechanism presented in the table below does not conform to SURFACE CHEMKIN formalism since surface sites are not conserved (see reactions 5-10).

![Figure 2-10: Temperature dependence of the desorption species formation from a \(W-O_2\) reaction, source: (Schissel and Trulson 1965).](image-url)
The study by Walsh et al. utilized the mechanism of Schissel and Trulson, as well as a detailed experimental study of high temperature tungsten oxidation rates to create an analytical surface coverage model for the reaction process (Walsh et al. 1967a). Walsh et al. took great care in their experimental setup and design to remove diffusion limitations of the reaction rates. This was especially important due to the high temperatures studied. Even with these considerations, diffusion limited reactions were found at the highest temperatures; however, they were able to extend the range of available kinetically limited data to greater temperatures than any prior study. Using the data, the empirical models of Perkins et al. were compared, and the mechanism of Schissel and Trulson was refined to create a predictive model. The model developed was much more complex that previous empirical models and is presented in Table 2-8.

Table 2-7: Tungsten and $O_2$ reaction mechanism from Schissel and Trulson (Schissel and Trulson 1965).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Chemical Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2\left(W_{(s)}\right) + O_2 \rightarrow 2\left(WO_{(s)}\right)$</td>
</tr>
<tr>
<td>2</td>
<td>$WO_{(s)} \rightarrow W_{(s)} + O$</td>
</tr>
<tr>
<td>3</td>
<td>$2\left(W^<em>_{(s)}\right) + O_2 \rightleftharpoons 2\left(WO^</em>_{(s)}\right)$</td>
</tr>
<tr>
<td>4</td>
<td>$WO^<em>_{(s)} \rightarrow W^</em>_{(s)} + O$</td>
</tr>
<tr>
<td>5</td>
<td>$2\left(WO^*<em>{(s)}\right) \rightarrow W</em>{(s)} + WO_2$</td>
</tr>
<tr>
<td>6</td>
<td>$WO_{(s)} + 2\left(WO^*<em>{(s)}\right) \rightarrow W</em>{(s)} + WO_3_{(s)}$</td>
</tr>
<tr>
<td>7</td>
<td>$WO_3_{(s)} \rightarrow WO_3$</td>
</tr>
<tr>
<td>8</td>
<td>$WO_3_{(s)} + W_{(s)} \rightarrow WO_2 + WO^*_{(s)}$</td>
</tr>
<tr>
<td>9</td>
<td>$2\left(WO_3_{(s)}\right) \rightleftharpoons (WO_3)_{2(s)} \rightarrow W_2O_6$</td>
</tr>
<tr>
<td>10</td>
<td>$3\left(WO_3_{(s)}\right) \rightleftharpoons (WO_3)_{3(s)} \rightarrow W_3O_9$</td>
</tr>
</tbody>
</table>
The model developed by Walsh et al. was found to predict their data with reasonable accuracy, particularly given the wide range of conditions studied. It was also determined that Eq. 2-15 from Perkins et al. adequately described their data as well; however, there was a considerable discrepancy found at the lower temperatures studied by Walsh et al.

Table 2-9 presents an outline of studies involving tungsten and carbon dioxide oxidation kinetics. The number of studies involving CO₂ is much less than O₂. In all of the studies presented, vaporized tungsten oxides are formed, creating a net loss of tungsten material.

Table 2-8: Tungsten-O₂ surface coverage reaction model from Walsh et al. (Walsh et al. 1967a).

\[
\begin{align*}
\dot{n}_{W-O_2} &= \left(\frac{k_{21}k_{32}}{k_{21} + k_{32}}\right) + \left(\frac{k_{31}k_{32}}{k_{31} + k_{32}}\right) \theta_1 \theta_2 + 2k_{26} \theta_1^2 \theta_2^4 + 3k_{39} \theta_1^3 \theta_2^6 = \frac{\text{moles of } W}{\text{cm}^2 \cdot \text{s}} \\
\theta_1 &= 1 + \left(\frac{k_3}{4vP}\right) - \left[1 + \left(\frac{k_3}{4vP}\right)\right]^2 \theta_1 = \frac{\left[\theta_1 + \left(\frac{k_5}{4vP}\right)\right] - \left[\theta_1 + \left(\frac{k_5}{4vP}\right)\right]^2 - \theta_2^2 \left[1 - \frac{k_4}{vP}\right]}{1 - \frac{k_4}{vP}} \sqrt{vP} = \text{impingement rate of } O_2 \left[\frac{\text{moles}}{\text{cm}^2 \cdot \text{s}}\right] = P_o \left(2\pi MRT\right)^{\theta/2} \\
k &= A \exp\left(-B/RT\right)
\end{align*}
\]

<table>
<thead>
<tr>
<th>Constant</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_3)</td>
<td>7.92 \times 10^3</td>
<td>1.44 \times 10^5</td>
</tr>
<tr>
<td>(k_4)</td>
<td>7.07 \times 10^3</td>
<td>9.70 \times 10^4</td>
</tr>
<tr>
<td>(k_5)</td>
<td>7.05 \times 10^5</td>
<td>1.20 \times 10^5</td>
</tr>
<tr>
<td>(k_{21})</td>
<td>5.12 \times 10^9</td>
<td>1.44 \times 10^5</td>
</tr>
<tr>
<td>(k_{22})</td>
<td>8.90 \times 10^5</td>
<td>1.11 \times 10^5</td>
</tr>
<tr>
<td>(k_{31})</td>
<td>3.22 \times 10^6</td>
<td>1.16 \times 10^5</td>
</tr>
<tr>
<td>(k_{32})</td>
<td>1.59 \times 10^{-2}</td>
<td>4.05 \times 10^4</td>
</tr>
<tr>
<td>(k_{26})</td>
<td>3.88 \times 10^5</td>
<td>1.05 \times 10^5</td>
</tr>
<tr>
<td>(k_{39})</td>
<td>3.12 \times 10^5</td>
<td>1.05 \times 10^5</td>
</tr>
</tbody>
</table>
Table 2-9: Summary of previous experimental $W$-$CO_2$ high temperature kinetic studies.

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(Olcott and Batchelor 1964)</td>
<td>$\sim P_{CO_2}$</td>
<td>1982 – 2871</td>
<td>10</td>
<td>Mass change ($\Delta (m_f - m_i)/\Delta t$); resistively heated filament</td>
<td>-</td>
<td>-</td>
<td>Additions of CO to $CO_2$ inhibits reaction significantly</td>
</tr>
<tr>
<td>(Aspinall 1965)</td>
<td>$\sim P_{CO_2}$</td>
<td>$\sim 1730 – 2600$</td>
<td>0.00017 – 0.00031</td>
<td>Mass spectroscopy; resistively heated filament</td>
<td>-</td>
<td>-</td>
<td>$WO_2$ was the primary desorption species, $WO_3$ was barely detectable</td>
</tr>
<tr>
<td>(Walsh et al. 1967b)</td>
<td>300 (static)</td>
<td>1927 – 3027</td>
<td>20 – 337 (stagnation)</td>
<td>Surface recession ($\Delta (x_f - x_i)/\Delta t$), high velocity jet impingement; inductively heated sample</td>
<td>79</td>
<td>0.88</td>
<td>Diffusion limited rates found @ high T (&gt;2377°C); small CO additions showed depressed rates; overall rates much less than $O_2$</td>
</tr>
<tr>
<td>(Harvey 1974a)</td>
<td>600</td>
<td>$2177 – 2727$</td>
<td>0.0162 – 0.097</td>
<td>Mass change ($\Delta (m_f - m_i)/\Delta t$), static flow; resistively heated sample</td>
<td>-</td>
<td>0.78 – 1.18</td>
<td>Diffusion limited rates found throughout</td>
</tr>
</tbody>
</table>
Walsh et al., the same research group to study the $O_2$ reaction system, studied the reactions involving tungsten and $CO_2$ as well, using the same experimental setup as previous. They also explored the effect of $CO$ on the oxidation process. Although $CO$ did not cause tungsten to oxidize and form volatile species, $CO$ to $CO_2$ ratios as high as 5:1 indicated a slight suppression of the $CO_2$ oxidation rates. The correlation developed by Walsh et al. is shown in Eq. 2-16. Walsh et al. also determined that $O_2$ was a much more efficient oxidizer than $CO_2$ and therefore exhibits much faster reaction rates. The suppression of the reaction between $CO_2$ and tungsten with $CO$ addition was observed by Batchelor and Olcott as well, although the effect was much more severe since $CO$ to $CO_2$ ratios as high as 62:1 were used (Olcott and Batchelor 1964).

$$\dot{r}_{W-CO_2,CO}^{\text{Walsh et al.}} = 2.19 \frac{\text{moles of } W}{\text{cm}^2 \cdot \text{sec} \cdot \text{torr}^{0.88}} \cdot \exp \left( \frac{-79 \text{kcal/mol}}{Ru \cdot T} \right) \cdot \left( \frac{P_{CO_2}}{P_{CO}} \right)^{0.88} \times \left[ 1 - 0.547 \left( \frac{P_{CO}}{P_{CO_2}} \right)^{0.5} \right]^{0.88} \cdot \exp \left( \frac{-14.7 \text{kcal/mol}}{Ru \cdot T} \right)$$

(2-16)

In unpublished work performed at the Union Carbide Research Institute (Aspinall 1965), Schissel and Trulson performed a MS study of the tungsten and $CO_2$ reaction using the identical setup that was used in the $O_2$ study (Schissel and Trulson 1965). The outcome of this work illustrated some interesting results describing the differences between the $CO_2$ and $O_2$ systems. It was expected that after the dissociative adsorption process, the reactions would proceed in nearly identical manners; however, the intensities of all desorbing species decreased with $CO_2$. Tungsten trioxide was a primary desorption species using $O_2$ as an oxidizer, but it was barely detectible when using $CO_2$, indicating a distinct difference in the two reaction systems. Schissel and Trulson theorized that the decreased reactions rates compared to $O_2$ are the fact that a different limiting reaction occurs during $CO_2$ oxidation. A definitive conclusion regarding the cause of this result was not realized; therefore their conclusions were not beyond question. An activated adsorption process was concluded to occur, as opposed to adsorbed $CO$ reducing the available reaction area. Evidence for this conclusion was provided by the fact that they saw no reduction in $O_2$ oxidation rates with a large addition of $CO$ into the system ($CO:CO_2 = 10$). The activated adsorption process would be Eq. 2-17.
### Table 2-10: Summary of previous experimental $W$-$H_2O$ high temperature kinetic studies.

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(Sasaki and Hamamura 1955; Hamamura 1959c; Hamamura 1959b; Hamamura 1960)</td>
<td>(assumed $= P_{H_2O} + P_{H_2}$)</td>
<td>997 – 2187</td>
<td>12.10^{-5} – 64.10^{-4}</td>
<td>$\Delta P$ of collected $H_2$ product gas; $W$ filament resistively heated in a flowing gas environment</td>
<td>~ 35 (ave.)</td>
<td>0.6 – 0.8</td>
<td>Reaction probability increases with T, but is low; @ high T and low P, $H_2$ inhibits oxidation; $WO_2$ was primary desorption species; however, the $O:W$ ratio increased with T up to ~4</td>
</tr>
<tr>
<td>(Farber 1959)</td>
<td>760</td>
<td>1412 – 1722</td>
<td>38</td>
<td>Resistance (R) change, assuming $\Delta R$ of resistively heated filament was proportional to area; external gas flow</td>
<td>14.5</td>
<td>-</td>
<td>Oxidation mass loss of $W$ samples were not appreciable below ~1327°C</td>
</tr>
<tr>
<td>(Olcott and Batchelor 1964)</td>
<td>~$P_{H_2O}$</td>
<td>1982 – 2871</td>
<td>15</td>
<td>Mass change ($\Delta (m_{m} - m) / \Delta t$); resistively heated sample</td>
<td>-</td>
<td>-</td>
<td>$H_2O$ reacts faster than $CO_2$, $H_2$ inhibits reaction significantly</td>
</tr>
<tr>
<td>(Aspinall 1965)</td>
<td>~$P_{H_2O}$</td>
<td>1627 – 2527</td>
<td>25 – 155</td>
<td>Surface recession ($\Delta (x_{m-x} / \Delta t)$, high velocity jet impingement; inductively heated sample</td>
<td>~ 60</td>
<td>0.7 – 0.9</td>
<td>Rate determining step consisted of oxidation of $WO_{2,0}$ to $WO_{3,0}$, and its polymers as well as $WO_{2}(OH)_2$</td>
</tr>
<tr>
<td>(Kilpatrick and Lott 1966)</td>
<td>Not stated (assumed $= 760$)</td>
<td>1000 – 1700</td>
<td>(assumed $= 760$)</td>
<td>Mass change ($\Delta (m_{m} - m) / \Delta t$); external gas flow past inductively heated sample</td>
<td>48.9 (low T)</td>
<td>22.7 (high T)</td>
<td>$H_2O$ reacts faster than $CO_2$, diffusion limited reactions at high temperatures, oxidizer pressure dependence decreases with T</td>
</tr>
<tr>
<td>(Harvey 1974b)</td>
<td>600</td>
<td>2177 – 2727</td>
<td>0.026 – 0.138</td>
<td>Mass change ($\Delta (m_{m} - m) / \Delta t$), static flow; resistively heated sample</td>
<td>-</td>
<td>1.2 – 1.3</td>
<td>Diffusion limited rates found throughout; reaction rates involving $H_2O$ were less than $O_2$, but greater than $CO_2$</td>
</tr>
<tr>
<td>(Andrievskii et al. 1981)</td>
<td>(assumed $= P_{H_2O} + P_{O_2}$)</td>
<td>1377 – 2223</td>
<td>7.5·10^{-4} – 2.25·10^{-3}</td>
<td>Radiometric method; $W$ plate resistively heated</td>
<td>-</td>
<td>0.25</td>
<td>Oxidation rate was ~4 – 6 times slower than w/ $O_2$, but faster than $CO_2$ $H_2O$ oxidation reaction</td>
</tr>
<tr>
<td>(Smolik et al. 1989; Smolik et al. 1990; Smolik 1992)</td>
<td>~$638$</td>
<td>600 – 1200</td>
<td>–319</td>
<td>Surface recession ($\Delta (x_{m-x} / \Delta t)$, mass change ($\Delta (m_{m} - m) / \Delta t$), and volatile product collection; external flow past inductively heated sample</td>
<td>31</td>
<td>1.0</td>
<td>Volatilization rates are fast with $W$, may create significant amounts of $H_2$</td>
</tr>
<tr>
<td>(Greene and Finfrock 2001)</td>
<td>760</td>
<td>700 – 1350</td>
<td>(assumed $= 760$)</td>
<td>Surface recession and mass measurements determined ($\Delta (m_{m} - m) / \Delta t$), ($\Delta (x_{m-x} / \Delta t)$, external flow past inductively heated sample</td>
<td>47.2</td>
<td>-</td>
<td>$W$ oxidation products vaporize above 800°C, stoichiometry of collected products was $WO_{2,3}$ indicating primarily $WO_2$ and $WO_3$ products</td>
</tr>
<tr>
<td>(Unal et al. 2000)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Unal et al. used data from (Kilpatrick and Lott 1966; Smolik et al. 1989; Smolik et al. 1990; Smolik 1992) to develop a correlation.</td>
<td>48</td>
<td>-</td>
<td>Unal et al. used chemical kinetic and diffusion theories, as well as experimental results from other researchers to develop a correlation.</td>
</tr>
</tbody>
</table>
A summary of previous experimental tungsten and water vapor reaction studies is presented in Table 2-10. Several of these studies were conducted recently in contrast to the other oxidation systems discussed. The water reaction has received recent interest due to the use of tungsten as a structural material in nuclear reactors and proton accelerator components.

The works by Farber and Hammamura et al. were completed during the infancy of the development of techniques for exploring the fundamental nature of high temperature heterogeneous reactions (Sasaki and Hammamura 1955; Farber 1959; Hamamura 1959a; Hamamura 1959b; Hamamura 1959c; Hamamura 1960). Conclusions drawn from these results are therefore restricted by the levels of uncertainty in their data due to the experiments used. However, both investigations yielded good phenomenological information regarding the tungsten-water reaction system.

Hamamura et al. concluded that the sticking probabilities of water molecules colliding with the surface are low due to low reaction probabilities. They also determined that $H_2$ may reduce reaction rates, much in the same manner that $CO$ was found to reduce the $CO_2$ reaction rates with tungsten. Both of these phenomena have been observed by Olcott and Batchelor (Olcott and Batchelor 1964). Lastly, Hamamura et al. determined that $O:W$ ratios of collected products increases with rising temperatures, indicating that multiple oxide or hydroxide species are formed, and relative quantities vary with temperature.

As in Harvey’s previous studies, diffusion limited reactions were found throughout (Harvey 1974b). Of qualitative importance, Harvey determined that reaction rates involving $H_2O$ are slower than $O_2$, but faster than $CO_2$, provided that the partial pressures of all three species are the same under the range of temperatures studied. This was also confirmed by Olcott and Batchelor.

Quets and Walsh explored the tungsten and water vapor reaction using the same stagnation flow experiment used to determine the oxidation kinetics involving $O_2$, $CO_2$, and $CO$ (Walsh et al. 1967a; Walsh et al. 1967b); however, for unknown reasons this work was not published, and appears only in a government report (Aspinall 1965). Like the other oxidizer systems, $H_2O$ reactions were diffusion limited at high temperatures, causing reduced
temperature dependence. At lower temperatures, where reactions were deemed to be
kinetically limited, an activation energy of 60 kcal/mol was found, which lies in between that
of \( \text{O}_2 \) and \( \text{CO}_2 \). For this reason, if the oxidizer partial pressures are constant, the reaction rate
of tungsten and \( \text{H}_2\text{O} \) are in between that of \( \text{O}_2 \) and \( \text{CO}_2 \). Quets and Walsh also determined an
oxidizer pressure exponent \((n)\) of 0.9 at 2000 K, which was reduced to 0.7 at 2800 K. However, it is unclear if the onset of diffusion limited reactions led to the change in the reaction rate’s water vapor pressure dependence.

Kilpatrick and Lott collected enough reaction rate data to determine a simple Arrhenius
reaction rate correlation to describe the oxidation process involving water (Kilpatrick and
Lott 1966). In their experiments two regions of varying temperature dependence were found,
as indicated by Eq. 2-18 \((T = 1050 – 1450^\circ\text{C})\) and Eq. 2-19 \((T = 1450 – 1700^\circ\text{C})\). Little
discussion was provided for the reduced temperature dependency at higher sample
 temperatures. A detailed discussion of the flow conditions within the reactor were not given,
however, it is surmised that the reduced temperature dependency at higher temperatures is
due to diffusion limited reactions. Kilpatrick and Lott concluded the rate determining step is
the oxidation of the surface dioxide, \( \text{WO}_2\text{(s)} \), to volatile tungstic acid \([\text{WO}_2\text{(OH)}_2]\), tungsten
trioxide \((\text{WO}_3)\) and its polymers. It should be noted that the low temperature correlation’s
pre-exponential factor is a factor of a thousand greater than presented in the original
publication, which is determined to contain a typographic error. This determination has been
made by other researchers (Unal et al. 2000; Greene and Finfrock 2001), and is verified by
comparing the correlation with the Kilpatrick and Lott’s published data. All tests were done
at 1 atm of \( \text{H}_2\text{O} \).

\[
\dot{\text{r}}_{\text{W-H}_2\text{O}}^{\text{(Kilpatrick and Lott)}} = 28.1 \frac{\text{moles of W}}{\text{cm}^2 \cdot \text{sec}} \cdot \exp\left(\frac{-48.9 \text{ kcal/mol}}{\text{Ru} \cdot T}\right) \quad (2-18)
\]

\[
\dot{\text{r}}_{\text{W-H}_2\text{O}}^{\text{(Kilpatrick and Lott)}} = 4.7 \times 10^{-3} \frac{\text{moles of W}}{\text{cm}^2 \cdot \text{sec}} \cdot \exp\left(\frac{-22.7 \text{ kcal/mol}}{\text{Ru} \cdot T}\right) \quad (2-19)
\]

Work completed by Andrievskii et al. provided support for some of the previous
studies (Andrievskii et al. 1981); however, quantitative models for water vapor oxidation
were minimal, and the results seemed to indicate that diffusion limited reactions may be
occurring. A better phenomenological perspective of the tungsten and water reaction was provided by Andrievskii et al. Results confirmed that $H_2$ inhibits the oxidation reaction, and also that the $H_2O$ reaction is faster than $CO_2$.

Much of the work presented by Kilpatrick and Lott was repeated by Greene and Finfrock (Greene and Finfrock 2001), studying the lower temperature range in more detail. Greene and Finfrock determined the formation of the gas-phase tungstic acid $[WO_2(OH)_{2(g)}]$, which has a high vapor pressure, causes the vaporization of any oxides formed on the tungsten surface. This causes tungsten to start to lose mass during oxidative corrosion at temperatures between 700 and 800°C. Using their data, Eq. 2-20 was created to describe the rate of vaporization. As with the previous study of Kilpatrick and Lott, Greene and Finfrock did not explore the pressure dependent properties of the reaction, and the equation below is valid only for a pressure of one atmosphere.

$$\dot{\nabla}_{W-H_2O} = 7.79 \frac{\text{moles of W}}{\text{cm}^2 \cdot \text{sec}} \cdot \exp \left( \frac{-47.2 \text{kcal/mol}}{R \cdot T} \right)$$  \hspace{1cm} (2-20)

Unal et al. used data from Kilpatrick’s study and Smolik et al. to develop an analytical model for the rate of tungsten consumption and hydrogen production at high temperatures in the presence of water vapor (Eq. 2-21) (Smolik et al. 1989; Smolik et al. 1990; Smolik 1992; Unal et al. 2000). Again no assessment of the water vapor pressure was made, however, the evaluation of data used in the correlation of Eq. 2-21 implied the assumption of a pressure exponent of unity. The primary focus of the Unal et al. and Smolik et al. studies was learning about possible failure mechanisms and hazards of plasma facing surfaces within a nuclear reactor.

$$\dot{\nabla}_{W-H_2O} = 31.4 \frac{\text{moles of W}}{\text{cm}^2 \cdot \text{sec}} \cdot \exp \left( \frac{-48.0 \text{kcal/mol}}{R \cdot T} \right)$$  \hspace{1cm} (2-21)

Other oxidizing species that have been examined are detailed in Table 2-11. Since many of these oxidizers are not present in large quantities in most systems the quantity and level of detail is limited. For these reasons they are not discussed in detail.
Table 2-11: Summary of previous experimental high temperature kinetic studies involving tungsten and less prominent oxidizers.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(Farber and Ehrenberg 1952)</td>
<td>≤760</td>
<td>900 – 1150</td>
<td>(H_2S, SO_2); ≤114</td>
<td>Resistance (R) change, assuming (\Delta R) of resistively heated filament was proportional to area; external gas flow</td>
<td>-</td>
<td>-</td>
<td>Tungsten resists significant corrosion in reducing atmosphere ((H_2S)), but readily oxidizes in (SO_2)</td>
</tr>
<tr>
<td>(Farber et al. 1955)</td>
<td>≤760</td>
<td>1107 – 1627</td>
<td>(NO); 38</td>
<td>Resistance (R) change, assuming (\Delta R) of resistively heated filament was proportional to area; external gas flow</td>
<td>60 (1107 – 1237ºC)</td>
<td>14.7 (1237–1627ºC)</td>
<td>Reaction rates controlled by the level of dissociation of (NO) to (O_2); at high T reaction rates are equal to (O_2) rates due to complete dissociation</td>
</tr>
<tr>
<td>(Rosner and Allendorf 1967b)</td>
<td>1</td>
<td>700 – 1350</td>
<td>(O); 0.001 – 0.05</td>
<td>Resistance (R) change, assuming (\Delta R) of resistively heated filament was proportional to area; external gas flow</td>
<td>4</td>
<td>-</td>
<td>Reaction probabilities found to be &gt;140 times than of molecular oxygen and are independent of (P_O).</td>
</tr>
<tr>
<td>(Meubus 1978)</td>
<td>≤760</td>
<td>1327 – 1827</td>
<td>(SO_2); ≤114</td>
<td>Mass change ((\Delta(m_f-m_i)/\Delta t)); resistively heated sample; external flow</td>
<td>-</td>
<td>-</td>
<td>Tungsten readily oxidizes in (SO_2)</td>
</tr>
</tbody>
</table>
2.3 Rocket Nozzle Erosion

The purpose of a rocket nozzle is to produce thrust (a forward directed force), which is generally accomplished by transferring the high temperature and pressure gases created from a combustion process into kinetic energy. The total thrust and efficiency of this transfer of energy is highly dependent on the nozzle geometry. A simplified expression for rocket thrust is presented in Eq. 2-22, given as a function of chamber pressure, nozzle throat area, and a thrust coefficient \( C_T \), which is a function of the specific heats of the gas mixture, nozzle throat and exit areas, and pressure drop across the nozzle. Relatively small changes in nozzle contours and throat area may drastic effect nozzle performance; therefore, minimization of nozzle erosion is a very important issue in motor performance. If the throat erodes, the throat area increases, causing the chamber pressure to drop off quickly – slowing propellant burning rates – reducing thrust. It is often deemed unacceptable to have increases in nozzle throat area of greater than 5%, and a change of greater than 10% may cause the loss of thrust control (Wong 1968). Since corrosion reactions are often strong functions of pressure and temperature, reductions in rocket motor operation times and conditions (i.e., temperature and pressure) are often required to limit erosion rates, which are typically between 0.01 and 0.25 mm/s at the throat.

\[
\text{Thrust} = C_T \cdot A_{\text{throat}} \cdot P_{\text{chamber}} \tag{2-22}
\]

Most nozzles used in propulsion applications have a conventional de Laval, or converging-diverging design. Hot gases enter the nozzle through the converging section, accelerating the flow. The gases continue to accelerate until reaching a “choked” condition (i.e., Mach number = 1) at the throat, the flow is then accelerated further to supersonic speeds in the diverging section. A schematic of a typical nozzle used in solid rocket motor is shown in Fig. 2-11. Theory and application of nozzles for propulsion may be found in several sources (John 1984; Sutton and Biblarz 2001; Zucker and Biblarz 2002).
Nozzle erosion mechanisms may be separated into two primary categories, chemical and mechanical erosion. Chemical erosion, or corrosion, is of primary concern in this study as it involves the chemical attack of gases from the combustion process. The chemical reactions occurring at the nozzle surface alter surface structure and composition, which leads to corrosion due to phase transformation or enhanced mechanical erosion due to a weakened surface. A schematic of nozzle corrosion mechanisms is shown in Fig. 2-12. In tungsten-based nozzles, the primary mechanism is the formation of volatile species due to the
oxidation of nozzle surface. Metal oxidation reactions are strongly dependent on temperature, therefore corrosion is generally greatest at the nozzle throat, where heat transfer between the hot combustion products and nozzle surface is greatest (Lafazan and Turnacliffe 1961; Heath and Thackray 1969).

During rocket motor operation, rates of corrosion may be limited by several mechanisms, including diffusion and chemical kinetics. After ignition, the combustion reaction quickly reaches steady-state in terms of operating temperature and pressure. For this reason, the composition of the hot products does not change considerably during motor operation. However, heating of the nozzle is generally a transient process, causing surface temperature to be a function of time as well as location. This may cause corrosion to be both kinetically and diffusion limited during motor operation, requiring detailed knowledge of product gas composition, mass and heat transfer rates, nozzle flow rates, boundary layer geometry, as well as chemical reaction kinetics in order to accurately predict nozzle erosion rates.

Mechanical erosion is caused by the high shear forces created by the flow of gases, as well as impact of solid and liquid particles entrained in the flow. This erosion mechanism is a concern when using metallized solid propellants. Aluminum (Al) is often added to solid propellant mixtures to increase energy densities (flame temperatures) and burning rates of
propellants. The $Al$ oxidizes forming aluminum oxide ($Al_2O_3$), which has a high melting and boiling point and can impact the nozzle surface at high speeds, causing pitting and cracking of the surface. Mechanical erosion lends itself to uneven erosion as well, which causes thrust misalignment and reduced performance. In tungsten nozzles it is also theorized that non-oxidized aluminum may impact an oxidized nozzle surface, causing a thermite reaction, which is a very exothermic reaction involving a metal and a metal oxide, Eq. 2-23 (Fischer and Grubelich 1998). This reaction may in turn cause localized heating of the nozzle surface, increasing the rate of corrosion.

$$2Al + Wo_3 \rightarrow Al_2O_3 + W$$

$$\Delta H_R = -2.92 \text{kJ/gram of react.} \left(-697 \text{cal/gm}\right)$$

$$4Al + 3WO_2 \rightarrow 2Al_2O_3 + 3W$$

$$\Delta H_R = -2.10 \text{kJ/gram of react.} \left(-502 \text{cal/gm}\right) \quad (2-23)$$

Given the erosion mechanisms mentioned, nozzle materials should possess several properties in order to maximize rocket motor performance. This includes: good heat resistance and capacity, resistance to thermal shock, high melting temperature, resistance to chemical attack by combustion products, high strength at high temperatures, and have low weight. These properties create an inherently thin ensemble of materials that may be used for such an application, and none possess all the desired qualities. Often these materials have high costs due to mining and refinement of raw materials (e.g., refractory metals such as $W$ or $Re$) or difficulty of manufacture (e.g., 3-D carbon composites). Tungsten possesses many of the properties required for a good nozzle material, but has been limited in application due to high costs, high mass, and susceptibility to chemical attack. Lightweight, inexpensive materials such as phenolic (plastic) composites reinforced with silica, carbon, nylon or graphite have been widely used with success; however, these materials are limited to lower operating pressures compared to refractory materials or carbon-carbon ($C-C$) composites. Further discussion of the nozzle design requirements and various materials may be found in several other sources (Bartlett 1963; Wong 1968; Heath and Thackray 1969; De Morton 1977; Hildreth 1987; Sutton and Biblarz 2001). An overview of graphite rocket nozzles and their associated chemical erosion processes is presented in Appendix A.
2.3.1 Review of Tungsten-Based Nozzle Erosion Studies

It appears that much of the experimental and theoretical studies involving tungsten-based rocket motors have been conducted for defense and space applications, and much of the literature is in the form of older U.S. government reports (Preston 1961; Ratliff et al. 1963; Schaefer et al. 1964; Johnston et al. 1966; Lake 1966; Winter et al. 1966; Price 1969; Wilson 1970). Only a few articles appear in journals or conference proceedings (Olcott and Batchelor 1964; Haugen 1998). The government reports primarily present evaluations of tungsten-based nozzle applications and performance, little discussion is devoted towards the underlying chemistry involved in the corrosion process. Only a small quantity of results may be found in open sources regarding erosion rates of tungsten-based nozzles. More recently, renewed interest in understanding nozzle erosion mechanisms have led to several, mostly theoretical studies involving tungsten erosion (Haugen 1998; Opeka 2001; Opeka 2004; Liggett and Menon 2007; Sabourin and Yetter 2007; Thakre and Yang 2008; Sabourin and Yetter 2009; Thakre and Yang 2009).

One of the government reports, a study by Johnston et al. of the NASA-Lewis Research Center, studied the erosion characteristics of several nozzle materials with three different propellant formulations with varying flame temperatures, oxidizer content, and product abrasiveness (Johnston et al. 1966). All testing was performed using sub-scale rocket motors. Nozzle throat erosion was estimated based on combustion chamber pressures, and post-test analysis of nozzle inserts. Tungsten-based nozzle materials were found to perform well, except with the propellant with the greatest oxidizer content (i.e., non-metallized propellants). This conclusion is supported and explained by various thermodynamics-based studies (Opeka 2004; Sabourin and Yetter 2007), of which the latter is summarized in Appendix B. Erosion rates were also found to be affected greatly by the material density. High density materials performed the best. In fact, acceptable amounts of erosion were found with all three propellant formulations using fully densified, arc cast tungsten produced at NASA. The disadvantage of this is the increased nozzle weight. Tungsten metal carbides were also studied, showing good erosion resistance although problems were encountered due to thermal stress cracking.
A separate published study also determined that oxidative chemical erosion and thermal stress cracking to be the two primary erosion mechanisms of tungsten-based nozzles (Olcott and Batchelor 1964). Olcott and Batchelor used laboratory scale testing of the reaction rates of pure tungsten at high temperatures, as well as analysis of post-fired tungsten nozzles to establish these conclusions. Discussion of the laboratory scale testing is discussed in the preceding sections. In addition to demonstrating that gas-phase composition may strongly affect corrosion rates, Olcott and Batchelor also measured erosion of \( W \) wires in direct contact with burning propellants. Aluminized propellants demonstrated the least amount of erosion, and surface analysis indicated some tungsten carbide formation. High density tungsten with large grain size achieved the greatest performance among the various tungsten nozzles considered. Results of these simple laboratory tests showed good phenomenological agreement with sub- and full-scale motor testing. Testing of alloyed tungsten with rhenium (\( Re \)) or thorium dioxide (thoria, \( ThO_2 \)) were shown to decrease corrosion rates; however, thoria is an unlikely candidate for use in rocket nozzles since it is radioactive. The greatest drawback found with the use of \( W \) in rocket nozzles was thermal stress cracking, which can cause pieces to break away, increasing mechanical erosion rates. The majority of this cracking is determined to occur at the beginning of nozzle firing due to the high thermal gradients created.

After substantial research and development of rocket nozzle materials through the 1970’s, tungsten-based nozzles have been reserved for larger motor applications using high thrust, aluminized solid propellants. Other materials that have been developed, such as advanced graphite and phenolic materials have become staples in nozzle designs. Tungsten and other materials are beginning to be studied in detail again in order to find ways of increasing motor performance.

Of the more recent studies, a research group from Norway has studied the erosion rates of various refractory metal materials using a small scale rocket motor (Haugen 1998). Results of this study, which used chlorine containing propellants of varying formulation, indicated the primary erosion mechanism to be oxidative corrosion. Although low rates were found with pure tungsten using the most corrosive propellant (0.02 – 0.03 mm/s), alloying of the tungsten with rhenium produced no erosion. This comes at an increased economic cost
and reduced material melting temperature, which limits applications. Tungsten nozzles were also found to erode much slower than pure molybdenum.

Recent advancement in computing power has drastically increased modeling and prediction capabilities of nozzle erosion rates. For this reason, the latest studies involving tungsten nozzle erosion have used computer modeling (Liggett and Menon 2007; Thakre and Yang 2008; Thakre and Yang 2009). In the study by Liggett and Menon, the development of a model capable of predicting mechanical and chemical erosion was presented. Several potential nozzle materials were compared, including a $W$-$Re$ alloy and a pure niobium ($Nb$) refractory metal. As in previous studies, the tungsten-based alloy erosion was predicted to be controlled almost entirely by chemical or thermal erosion mechanisms, whereas the softer $Nb$ material displayed significant erosion due to particle impacts. Based on these results, it was concluded that $W$-based nozzle erosion may be reduced by cooling the nozzle surface to reduce reaction rates, with little regard to minimizing mechanical mechanisms. The high shear nozzle flow was predicted to play a negligible role unless melting temperatures are approached with all materials considered.

The modeling studies of Thakre and Yang considered solely the chemical erosion mechanism of tungsten, rhenium, and molybdenum nozzle materials. Considering only $CO_2$ and $H_2O$ oxidizing species, kinetically limited erosion rates were found, with $H_2O$ being the more reactive species. Molybdenum was determined to be the best performing nozzle material at low temperatures; however, it is limited by its lower melting temperature. Rhenium was found to perform better than $W$. Tungsten was demonstrated to exhibit lower nozzle throat recession rates than graphite, even though mass consumption rates were higher due to the large density differences in materials. The drawback of these studies is that they rely heavily on the kinetic reaction rate data from several unconnected studies, providing little continuity in the data. Additionally, these works rely on a limited pool of data and knowledge regarding the details of tungsten oxidation.
Chapter 3

EXPERIMENTAL APPROACH

In this chapter, the experimental technique used to determine high temperature reaction rates of tungsten is presented. Most of the methods available at the present time measure global oxidation rates in terms of either the total oxidizer uptake or changes in mass or dimension of the base material over time. Many of these methods are described in Chapter 2 (2.1.1). Due to the unique thermodynamic relationship between tungsten and its oxides, where vaporization temperatures of the oxides are much less than the base metal, global high temperature oxidation rates can be easily obtained by measuring the mass loss as function of time and temperature. This method is termed thermogravimetric (TG) analysis. Advantages of this technique are: simultaneous and continuous mass recording as a function of time, precise control of gas-phase atmosphere, and the ease in which raw data may be interpreted and transformed into useful kinetic data with a minimal degree of uncertainty.

The following section presents the design, validation, and analysis approach taken in the development of the TG apparatus used in this study. The primary disadvantage of this method, which is a problem with all methods used to date, is that reaction rates are often so great that diffusion limited reactions are found. Another disadvantage is that the gas-phase reactants are heated along with the metal sample, which can lead to homogeneous reactions, altering the gas composition, making the reactants difficult to control.

3.1 Thermogravimetric Analysis

The oxidation kinetics of bulk tungsten were obtained under isothermal conditions by measuring the weight change over time using a TG analyzer (TGA) developed at The Pennsylvania State University (PSU). The primary components of the TGA are a Cahn D-101 digital recording balance (Thermo Electron Corp., Newington, NH), a vertical tube furnace (Applied Test Systems Inc., Butler, PA), which had a maximum temperature of 1700°C, and a series of Teledyne Hastings Instruments (Hampton, VA) mass flow controllers.
(200 Series) used to regulate the flow of each gas through the system. A picture of the TGA is shown in Fig. 3-1, while a schematic of the TGA is presented in Fig. 3-2.

Figure 3-1: High temperature TGA developed at PSU.
3.1.1 Design Approach

Before beginning the design process, a set of goals were established in line with the motivation of this work. In the simpliest terms, a TGA is a flow reactor that simultaneously monitors time, temperature, and changes in mass in a controlled environment. Experimentally, several pieces of equipment were needed to meet these requirements, a means of: measuring changes in sample mass, controlling sample temperature, monitoring system temperature, controlling reactants that come in contact with sample, and recording the
temperature, mass, and time simultaneously. Given these requirements, a consultation with an individual who had designed an built TGAs (Fox 2005), and a initial review of high temperature oxidation (Kofstad 1988; Birks et al. 2006), the preliminary design goals were to:

1. Continuously measure sample masses as large as 10 grams with a minimum accuracy of ±100 µg as a function of time.
2. Control sample and atmospheric temperatures up to a minimum of 1700ºC and maintain isothermal conditions for extended times.
3. Accurately measure sample temperatures as a function of time over the entire TGA temperature range.
4. Control atmospheric conditions using a minimum of three separate gas species.
5. Simultaneously monitor, control, and record sample mass and temperature, as well as time and atmospheric conditions.
6. Use reactor materials that perform appropriately at high temperatures in both reducing and oxidizing atmospheres.
7. Operate with the utmost care to maintain safe operating conditions for the TGA equipment and operators (i.e., avoid gas leaks, combustion reactions).

With this outline, primary components of the TGA were researched and chosen to fulfill these goals as best as possible. Although all of these goals were reached in the design and construction processes, several concessions were made, mainly due of material and safety concerns. Due the high temperature and oxidizing atmospheres desired, many high temperature materials could not be used as components in the TGA.

3.1.2 System Components

The Thermo Cahn D Series digital recording balances were designed particularly for applications such as TGA, providing high sensitivity and a hanging sample design. Additionally, Cahn balances were intended to record mass as a function time while connected to a computer at a maximum frequency of 1 Hz, and can be calibrated and tared using a computer as well. In this application, the Thermo Cahn D-101 was selected, which had a
maximum capacity of 100 grams and a maximum sensitivity of 1 µg over a range of ±1 gram. This balance exceeded the initial design goals.

After review of potential heat sources for the TGA, a tube furnace using molybdenum disilicide (MoSi2) heating elements was selected due to its versatility, cost, and maintainability. The furnace used for the TGA was an Applied Test Systems Series 3310, 6500-Watt tube furnace. The furnace was 21 inches long, 14 inches in diameter, and used six Kanthal Super 33 elements. The controller was a Barber Coleman Model 2404 with over temperature protection. The primary drawback of the furnace was that maximum temperatures were limited by material restrictions of components such as the furnace process tube and sample hangers. Materials that are non-reactive in oxidizing atmospheres are very limited at high temperatures. Some of these materials are shown in Table 3-1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density [g/cm³]</th>
<th>~ Melting Temperature [ºC]</th>
<th>~ Maximum Use Temperature (no load) [ºC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina (&gt;96% Al₂O₃)</td>
<td>3.80 – 3.92</td>
<td>2050 – 2322</td>
<td>1700 – 1800</td>
</tr>
<tr>
<td>Quartz (SiO₂)</td>
<td>2.20</td>
<td>1680 – 1978</td>
<td>1100 – 1400</td>
</tr>
<tr>
<td>Mullite (3 Al₂O₃ · 2 SiO₂)</td>
<td>2.80 – 3.03</td>
<td>1810</td>
<td>1650 – 1725</td>
</tr>
<tr>
<td>Sapphire</td>
<td>3.98</td>
<td>1800 – 1950</td>
<td>2050</td>
</tr>
<tr>
<td>Zirconia (ZrO₂ w/ various additives)</td>
<td>5.92 – 6.08</td>
<td>–</td>
<td>1500 – 2200</td>
</tr>
<tr>
<td>SiAlON (Silicon Aluminum Oxynitride)</td>
<td>3.24</td>
<td>–</td>
<td>1200</td>
</tr>
<tr>
<td>Porcelain</td>
<td>2.40</td>
<td>–</td>
<td>1400</td>
</tr>
</tbody>
</table>

*Property values vary with method of manufacture, size and shape of part, as well as purity. Values taken from several thermochemical handbooks and manufacturer references: (Bengisu 2001; CoorsTek 2008; McDanel 2008; TechnicalGlass 2008).

Based on material limitations, a high purity alumina (99.8%) tube was used as the furnace reactor tube. The 44 inch long tube had a 7/8 inch outside diameter and a 5/8 inch internal diameter. Sample hangers were constructed from thin (425 µm O.D.) sapphire fibers produced by Photran, LLC (Poway, CA), which may be manipulated to form hooks, and are strong, as well as flexible (Fig. 3-3).
Similar materials issues were of large concern when selecting a method of measuring the sample temperature. Thermocouples are the ideal method for measuring temperature due to their simple operation, cost, and ease in which temperatures are monitored and recorded. However, since both oxidizing and reducing atmospheres were expected to be used, there was no thermocouple that could measure temperatures as high as 1700ºC and resist these conditions. Tungsten-rhenium thermocouples (type C, D, G) measure temperatures up to 2320ºC, but do not handle oxidizing atmospheres (Omega 2008). Alternatively, platinum-rhodium thermocouples have a temperature range of as high as 1768ºC, but weaken at high temperature in reducing atmospheres. To combat these problems, a type D thermocouple with an accuracy of 1.0% was used along with a high purity alumina protection tubewell. This tubewell was filled with inert argon gas, protecting the thermocouple from high temperature oxidation. The drawback to the use of the tubewell was reduced sensitivity to changes in system temperature; however, the TGA was designed to be used under predominately isothermal conditions. Experience has shown that even with this protection tubewell, the alumina will degrade overtime due to reactions with tungsten and tungsten oxides, requiring the thermocouple to be replaced periodically.

At this point, design goals 1, 2, 3, and 6 were reached, with some compromises made regarding maximum system temperatures. All results found using the TGA were therefore extrapolated to predict reaction rates greater than 1700ºC. One of the last two goals of the TGA design were the ability to run a minimum of three different species of gases simultaneously into the system. This was accomplished using Teledyne Hastings 200 series mass flow controllers (MFCs). These controllers allowed for volumetric flow rates of nearly all commercially available gases to be accurately monitored and regulated – ±1% of full-scale range – over flow ranges as low a 0-10 standard cubic centimeters per minute (sccm), to as high as 0-500 standard liters per minute (slpm). Low scale ranges were needed in order to control oxidizer concentrations with a high degree of accuracy, while large-scale ranges...
were needed for inert carrier gases to reduce boundary layer thicknesses by maintaining a high flow rate of gases through the reactor. The TGA was designed so that an unlimited number of flow control devices could be used, but there were only two inlet options into the reactor (Fig. 3-4). Inert or non-reacting gases were always directed through the balance to ensure that no reactive species could contact any of the precision components or circuitry. Reactive or corrosive gases entered the system downstream of the balance.

In order to control and monitor the MFCs, a Teledyne Hastings four channel power supply (THPS-400) was used. This power supply had RS-232 communications, allowing it to be connected to a computer, providing control and monitoring capabilities of up to four flow controllers. Using LabVIEW (Laboratory Virtual Instrumentation Engineering Workbench) software and a data acquisition board (National Instruments PCI-6014), a program was designed and created that allowed for control of the gas flow through the

![Figure 3-4: Inlets to the TG flow reactor.](image)
system as well as control of the Chan balance. Additionally, system temperature, gas flows, mass, and time were monitored and recorded to a spreadsheet.

Due to the high temperatures employed for this experimental study reaction rates become appreciable, even under very low oxidizing species partial pressures. To combat this, commercially available ultra-high purity (UHP, ≥ 99.994%) gases were used for all inert carrier (helium, \(He\)) and reducing gases (\(H_2\)). This ensured that during any cleaning (reducing), pre- or post-test operations the sample was oxidized minimally. Purity of \(He\) and \(H_2\) gases was further increased by running gas lines through a liquid \(N_2\) purification trap. This condensed out trace amounts of \(H_2O\) and/or \(O_2\) from the gases.

### 3.1.2.1 Steam Generator

Water vapor is one of the most abundant oxidizing chemical species in solid rocket motor systems used today. Additionally, along with \(CO_2\) and \(O_2\), \(H_2O\) is one of the most important oxidizers in many combustion systems. However, due to the unique properties of water, it is often difficult to experimentally study the kinetics involving \(H_2O\) oxidation. An advantage of the TGA used in our work is that both the gas environment and the solid tungsten sample are heated during operation, reducing many of the concerns regarding vapor condensation within the reactor.

A flow of high purity \(H_2O\) was created and controlled by placing a \(H_2\) and \(O_2\) flow reactor upstream of the TGA (Fig. 3-5). Ultra high purity \(He\), \(H_2\) and \(O_2\) were brought separately into a 12 inch long horizontal tube furnace (Lindberg Model 55013, Watertown, WI) held at 690°C – well above the spontaneous ignition temperature of \(H_2\) (Glassman and Yetter 2008) – reacting the mixture within a ½ inch O.D. quartz or alumina reactor tube. A high purity alumina tube was required when producing more than about 300 cm³ per minute of steam due to the high levels of heat release produced by the combustion reaction. Oxygen was emitted at the center of the reactor tube through an internal alumina tube, while a mixture of \(He\) and \(H_2\) flowed concentrically over the internal oxidizer tube. The flow rates of \(H_2\) and \(O_2\) were controlled by electronic mass flow controllers, while a constant \(He\) flow rate was maintained using a rotameter. After formation of steam in the reactor it was flowed through stainless steel tubing that was held above the saturation temperature until it mixed
with the $He$ carrier gas stream at the top of the TGA’s furnace tube. The temperatures at this point were also maintained above the saturation temperature to remove any possibility of condensation. A 3-way valve allowed steam to bypass the TG reactor during system warm-up, and between test runs.

Figure 3-5: Diagram of the TGA’s $H_2O$ Generator.
System checkout indicated that the steam generator required an equivalence ratio slightly greater than unity to react all $O_2$ (see Fig. 3-6). At a critical minimum value, reaction rates increased rapidly due to the presence of $O_2$ in the system. As equivalence ratios increased above unity, reaction rates decreased due to the presence of $H_2$, which inhibits oxidation rates. For all subsequent testing, unless otherwise noted, a reactor equivalence ratio of 1.2, or a product $H_2O$ to $H_2$ ratio of 5:1 was used to guarantee no $O_2$ would be available to react with the sample.

The primary difficulties of this setup were ensuring that the water vapor did not condense prior to the reaching the furnace. The temperature of the $H_2O$, $H_2$, and $He$ mixture was maintained above the saturation temperature, but lower than any temperatures that could harm O-ring seals by wrapping the stainless steel tubing and the ceramic furnace tube with heating ropes and tapes (Omega Engineering Inc., Stamford, CT), and ceramic fiber insulation. Wall temperatures were checked periodically using a specifically design spring loaded surface thermocouple probe (Model SMP-HT-K-6, Omega Engineering Inc., Stamford CT) to make sure they remained within the required range.

![Figure 3-6: Effect of the steam generator’s operating equivalence ratio.](image)

**Figure 3-6:** Effect of the steam generator’s operating equivalence ratio.
3.1.3 Testing Procedures

Prior to all testing, the Cahn balance was calibrated using the MicroScan software provided by the balance manufacturer (ThermoCahn 2001). Calibrations were generally completed using a 100 mg calibration standard. At the onset of each test, the bulk material sample was hung from the balance within the furnace using a series of nichrome wire and sapphire suspensions. Multiple suspensions were used for several reasons, ease of handling and the removal of noise from the mass measurements. The multiple linkages damped out the movement of the sample created by the flow of gases over the suspension and sample surfaces. The samples were made of a thin bulk material, cut to any length. The width of the sample was limited to 0.35 inches so that it fit easily within the ceramic reactor tube, while avoiding contact with the tube walls. Each sample had a small, 1 mm diameter hole drilled at one end, which allowed it to hang securely from the sapphire suspensions. A schematic of a typical sample is shown in Fig. 3-7. Due to the overall length of the furnace tube, precise alignment between the hangers and furnace tube was required. Through trial and error over the course of this work it was determined that hanging a small diameter chemiluminescent glow stick from the balance into the furnace at room temperature using a strand of nylon monofilament was the best method to ensure proper alignment.

Figure 3-7: Typical test sample used with the PSU TGA.
Once the sample was loaded, all reactor connections were sealed, eliminating any means of access for the ambient room atmosphere to interact with the sample. The TGA system was flushed for a minimum of five minutes using $He$ and $H_2$ gas. This step not only flushed the balance and reactor, but also the gas lines and purification system leading to the TGA. After five minutes, liquid $N_2$ was added to the purification system dewars (Fig. 3-8), and the exhaust was ignited to burn the $H_2$. Flushing the reactor was required prior to this ignition process to ensure the mixture did not flashback into the reactor, potentially damaging the system or harming laboratory personnel. Liquid $N_2$ purification helped condense any oxygen or water vapor within the copper condensing coil, which was located upstream of the MFCs.

![Figure 3-8: TGA liquid nitrogen purification system.](image)

Once the liquid $N_2$ was added, the system was flushed two additional minutes before shutting off the $He$ flow, and regulating $H_2$ flow to 1 slpm or less. Under this reactor flow, the TGA’s furnace preheating cycle was initiated. The TGA was ramped up in temperature at a controlled rate of 25ºC per minute, which ensured no damage was done to the furnace or reactor components due to rapid heating. The furnace controller used B-type thermocouples ($Pt – 30\% Rh$, 1820ºC maximum use) mounted within the furnace (outside reactor tube) to monitor and control the furnace temperature. Once the desired system temperature was reached, the reactor was allowed to stabilize for a minimum of 5 minutes before testing.
Prior to each test, $H_2$ flow was removed from the reactor and replaced with pure $He$. The $He$ was then regulated to the desired overall test flow rate. The flow rates during testing were generally high, and often several minutes were required to stabilize the weight of the sample measured by the balance. When the weight stabilized, the balance was tared, and the desired flow rate of oxidizer was added to the system. To maintain the same overall system flow rate, $He$ flow was reduced to compensate for the oxidizer flow. This transition in flow generally caused a spike in the sample mass, however, the balance output quickly stabilized. The entire process was monitored, controlled, and recorded at a sampling rate of 1 Hz using the LabVIEW program. Tests lasted as little as 20 seconds in duration to more than 5 minutes, depending on the oxidizer type and concentration, perturbation of flow rates (i.e., required stabilization period), and reaction temperature. To stop the test, oxidizer flow was shutoff and replaced by $He$. Since the tungsten sample was consumed at high temperatures, the total mass loss of the sample was limited to ensure several tests could be performed using one sample. Changes in the overall sample dimension during testing were estimated based on the initial and final dimensions of the sample, and mass loss which occurred during each individual test run. Reaction rates were determined by the slope of the mass loss curve over time ($dm/dt$). Examples of these curves are shown in Fig. 3-9. The initial increase in sample consumption corresponds to the initiation of oxidation reactions as well as the time required by the flow controllers to reach steady state. The linear region corresponds to the steady-state reaction rate, which is a function of oxidizer type and concentration, temperature, and the sample’s surface area. The second rate transition corresponds to the removal of oxidizing species from the system. The degree of noise related to changing reactor flow is not noticeable in Fig. 3-9 since the overall flow rates are low and the $O_2$ partial pressure is small. At higher partial pressures and flow conditions, the transition was very noticeable.
3.1.4 Experimental Validation

To ensure that accurate and reproducible kinetically controlled global reaction rates could be determined using the TGA, a series of validations were completed. Kinetically controlled reactions are limited by the rate at which reactions may proceed given required energy barriers. Reactions may also be controlled by the diffusion of reactants, which must come into contact and adsorb onto the surface before reaction can occur (see Appendix C for diffusion limited reaction details). High temperature reactions are often diffusion controlled due to high reaction rates. In the case of the TG flow reactor, a boundary layer was created as the gas mixture flowed over the sample surface. This boundary layer was created by the adsorption and subsequent reaction of the oxidizer, creating a concentration gradient, as well as production of gas-phase metal oxides, which diffused away from the surface. To increase the concentration gradients of oxidizing species, which increases diffusion rates, the
boundary layer should be as thin as possible, and the surface should be flushed of gas-phase products. Within the TG reactor, this was accomplished by using high flow rates. Prior to running a new oxidizer and bulk material system, the minimum flow rate within the system was determined in order to achieve a kinetically limited reaction. This was done by simply running the system at maximum temperature over a range of total reactor flow rates. Examples of this are shown in Fig. 3-10. With the tungsten and \( O_2 \) system, above a flow rate of 20 slpm it was found that sample temperatures began to decrease slightly, which was why reaction rates dropped off. However, the results indicate that the reaction rate nearly approached the kinetically limited rate. Since the highest temperature was the worse case scenario, at lower temperatures kinetically limited reactions were easier to evaluate. In the tungsten-\( O_2 \) reaction system, minimum flow rates were determined to be 15 slpm, or a maximum of 20 slpm. In the tungsten-\( H_2O \) system it appeared that kinetically, or nearly kinetically limited reaction rates were found at all flow rates considered as the reaction rates were independent of the flow rate. For subsequent testing a flow rate of 12 slpm was used. The slower reaction rates of the \( W-H_2O \) system compared to the \( W-O_2 \) system were also demonstrated in the plots. Similar results were found for the slower rate \( W-CO_2 \) system, where it was determined that a reactor flow rate of 7 slpm was required to produce kinetically limited rates. At all flow rates considered, assuming entirely \( He \) flow, calculated tube Reynolds number (\( Re_D = \frac{\rho v D}{\mu} \)) indicated a laminar flow situation under all conditions studied. Typical \( Re_D \) values were calculated to be 20 – 60 at high temperatures; \( Re_D \) is inversely proportional to temperature since the gas density decreases and the viscosity increases with temperature. Further details regarding fluid dynamic and species concentration properties in the flow reactor may be found in Appendix C – diffusion limited heterogeneous reactions.

Global oxidation reactions may also be limited by adsorbed species migration, as described in Chapter 2. These cases may not be determined using the TGA. However, it is assumed that these cases only occur under extremely low pressure situations.
Selection of appropriate sample dimensions was also important. Samples are ideally as thin as possible to eliminate edge effects, where mechanical cutting and shearing can lead to increased reactions rates (Baur et al. 1956), as well as increased fluid dynamic drag forces on the foil, affecting weight measurements. Foils that erode too quickly decrease the number of tests that may be run per sample, and cause significant changes in surface area over a testing period (Fig. 3-11). To combat this, all testing and reported reaction rates used initial sample thicknesses of 200 µm and 300 µm.

Figure 3-10: Reaction rates as a function of reactor flow rates, (a) $O_2$ oxidizer, and (b) $H_2O$ oxidizer.

Figure 3-11: Effect of tungsten sample thickness over a series of oxidation tests.
Using oxidized 200 µm tungsten foils, the taper of the foil thickness was also studied to determine the extent of tapering, and to validate the assumption that surface area of a single sample may be assumed constant for all tests. Figure 3-12 shows the tapering of a tungsten foil at the conclusion of testing. The images show that there is a taper to the foils, particularly at the leading edge. This was due to the stagnation point at the leading edge, and because the boundary layer thickness was thinnest at this location. All these foils were oxidized using $O_2$ as an oxidizer, in cases where $CO_2$ and $H_2O$ oxidizers were used the taper was not as pronounced. It is interesting to note that the trailing edge appears to have a slight taper as well. Even with the tapering of the foil, it was still valid to neglect changes in foil thickness since the large facial areas of the foil make up at least 95% of the overall foil surface area.

![Figure 3-12: Tapering of tungsten foil during oxidation testing in $O_2$.](image)

Another validation of the TGA’s ability to accurately determine heterogeneous reaction rates was to confirm that different overall sample surface areas could be used. Three different samples were considered, two had the same surface area with different aspect ratios, while the third had a different surface area. A series of tests involving these samples were
conducted, illustrating reproducible results to within 10% (Fig. 3-13). This validates the conclusion that reaction rates, when normalized by surface area \(i.e.,\) grams, moles, or atoms per \((cm^2\text{-sec})\], are independent of surface dimensions used.

The final TGA validation, and most important was confirming that the measured changes in sample mass had low degrees in uncertainty. Part of this validation was maintained in the testing procedures by calibrating the balance prior to each test. It was determined that the balance maintains its calibration very well over time as long as it was not powered down; however, calibration procedures were still taken prior to testing regardless of when the balance was powered on or off. During testing, the changes in sample mass were recorded during each run. The total estimated sample mass loss during testing was then compared with the measured pre- and post-test sample masses. In each case where this was done, differences in between the measured and estimated changes in sample mass were an average of 4.4%, with a maximum deviation of 14%. These differences may be associated with changes in mass in between test runs due to impurities, as well as uncertainty in mass loss estimations; therefore, a high degree of certainty was associated with the measured mass changes during test runs.
3.1.5 Reaction Rate Analysis

As illustrated in Fig. 3-9, the TGA produces mass measurements of the sample as a function of time. The linear slope of these curves corresponded to the reaction rate of the bulk material \( b \) in terms of grams per second (\( \dot{g}_b \)). This information is presented formally by modifying the rate to account for surface area, and molecular weight of the bulk material using Eq. 3-1a-c, where \( i_b \) is the overall bulk material consumption rate per unit area, \( A_s \) is the surface area, \( MW \) is the molecular weight, and \( N_A \) is Avogadro’s number.

\[
\dot{i}_{b,\text{mass}} = \frac{\dot{g}_b}{A_{s,b}} \left[ \text{g mols} \right] \frac{\text{grams}_b}{\text{cm}^2_b \cdot \text{sec}}
\]

\[
\dot{i}_{b,\text{molar}} = \frac{\dot{g}_b}{A_{s,b} \cdot MW_b} \left[ \text{mol}_b \right] \frac{\text{mols}_b}{\text{cm}^2_b \cdot \text{sec}}
\]

\[
\dot{i}_{b,\text{atomic}} = \frac{\dot{g}_b \cdot N_A}{A_{s,b} \cdot MW_b} \left[ \text{atoms}_b \right] \frac{\text{atoms}_b}{\text{cm}^2_b \cdot \text{sec}}
\]

Assuming that heterogeneous reaction rates can be described using the Arrhenius rate equation described by Eq. 2-5, and including a oxidizer pressure dependence, an Arrhenius kinetic correlation is produced (Eq. 3-2), where the subscripts \( g \) and \( b \) represents the gas-phase and bulk metal reaction species, respectively. Using Eq. 3-2, the overall activation energy, pressure dependence, and pre-exponential factors can be determined for each reaction system through manipulation of the TG data. The activation energy, \( Ea \), is determined by plotting \( \ln(\dot{r}) \) verse \( 1/T \), producing a slope equal to \(-Ea/Ru\), where \( Ru \) is equal to 1.986 kilocalories per mole (8.314 kJ/mol). Similarly, reaction rate pressure dependence can be determined by plotting \( \ln(\dot{r}) \) verse \( \ln(P_{ox}) \), producing a slope equal to \( n \) (i.e., oxidizer pressure dependence). Finally the gas-solid reaction rate pre-exponential factor can be estimated by plotting \( \ln\left(\dot{r}/P_{ox}^n\right) \) verse \( 1/T \), where the y-axis intercept \((1/T = 0)\) is \( A \).

This information allowed a simple heterogeneous reaction system to be described under a wide range of conditions using a one-step kinetic reaction mechanism.

\[
\dot{i}_{b-g} = k_{b-g} \left( P_s \right)^{n_{b-g}} = A_{b-g} \cdot \exp\left( \frac{-Ea_{b-g}}{Ru \cdot T} \right) \cdot \left( P \right)^{n_{b-g}}
\]
Chapter 4

MODELING AND THEORETICAL APPROACH

In this chapter, the approaches taken to identify key elements in the tungsten oxidation mechanism using theoretical and computational methodologies are presented. Much of this work pertains to the approach outlined in Fig. 2-6. The first section presents tools used to identify important species in the mechanism. This is followed by a presentation of the numerical model used to model the thermogravimetric (TG) flow reactor. The governing equations, model geometry, and assumptions are given. Finally, methods for examining and predicting homogeneous and heterogeneous reaction mechanisms are provided.

4.1 Identification of Important Species and Reactions

Using current knowledge of heterogeneous reactions, the development of chemical reaction mechanisms used to describe reaction pathways and kinetics must be accompanied by experimental investigations. Experiments provide important information about the reaction mechanism as well as rate limiting reaction steps. They also provide a basis for the comparison of theoretical models. As stated by Kofstad:

“However, the mere use of reaction rates and kinetics is not a sufficient basis for interpreting reaction mechanisms; it is equally necessary to identify the reaction products, to characterize their formation, and to determine the microstructure of both the oxidized metal and the surface oxide (Kofstad 1966).”

Although Kofstad was referring to an oxidation system in which the bulk metal was oxidized, forming a solid scale, the message applies to all metal oxidation processes. Just as important are initial and intermediate species. The first step in the development of any kinetic reaction mechanism is to determine all species occurring over the course of a global reaction. These include reactants, products, and intermediate species needed to describe the reaction progression. Of most importance are the reactants and product species. The number of intermediate species and reactions depend on the complexity of the reaction, as well as the
level of detail, and often the accuracy required for the application of a given mechanism. Reactants are easily identified in most reaction systems; however, intermediates and products species are often unknown or uncertain. The intermediates are especially difficult to identify experimentally, particularly in high temperature and pressure systems. For this reason theoretical techniques must be used.

The most frequently used and thought of oxidizer is oxygen due to its large presence in air, and chemical simplicity. In combustion and energy systems, water and carbon dioxide are also very common oxidizers. Due to these reasons, $O_2$, $O$, $CO_2$, $H_2O$, and $OH$ are expected to be primary oxidizing species of interest.

In some cases, intermediate and product oxidation species may be determined by examining previous experimental studies. This is true when examining mass-spectroscopic (MS) studies of the tungsten and oxygen reaction (Berkowitz-Mattuck et al. 1963; Schissel and Trulson 1965; Azens et al. 1995). However, this $W$ and $O$ system does not account for many of the possible species that may form in a complex mixture. Due to the high temperatures and pressures considered in this study, reaction rates are generally very fast. This causes the chemical reaction system to reach, or nearly reach its equilibrium state rather quickly. Thermodynamic equilibrium calculations may then be employed to estimate product species, even in a flowing system. There are several software packages available that enable these calculations to be completed with great efficiency (McBride and Gordon 1996; Fried et al. 2004). Additionally, in the case of tungsten nozzle corrosion, potential oxidizers may be identified by predicting combustion products of propellants with equilibrium calculations.

As a caveat, these calculations are purely an estimation of potential product species present, particularly under high-speed gas flow. Moreover, these calculations are only as accurate as the thermodynamic parameters used to describe each species. Most software packages come with a standard thermodynamic database of species, it is up to the user to verify that all the required species and parameters for a given calculation are present. Using available tabulated data from two different sources, potential tungsten containing species were identified and shown in Table 4-1 (Chase 1986; Knacke et al. 1991). The majority of the species are tungsten oxides, carbides, chlorides, or oxychlorides. Noticeably missing from the database are nitride species of tungsten, these are predicted to form in very small to
negligible quantities under the conditions used in this study, and kinetics of such reactions are assumed to be slow compared to oxidation reactions.

Table 4-1: Tungsten species used in chemical equilibrium calculations.

<table>
<thead>
<tr>
<th>Condensed Phase Species</th>
<th>Gas-phase Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>W&lt;sub&gt;(cr)&lt;/sub&gt;</td>
<td>W</td>
</tr>
<tr>
<td>W&lt;sub&gt;(liq)&lt;/sub&gt;</td>
<td>W&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
<tr>
<td>WC&lt;sub&gt;(cr)&lt;/sub&gt;</td>
<td>W&lt;sub&gt;(cr)&lt;/sub&gt;</td>
</tr>
<tr>
<td>W&lt;sub&gt;2C&lt;/sub&gt;&lt;sub&gt;(cr)&lt;/sub&gt;</td>
<td>WO&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>WCl&lt;sub&gt;(g)&lt;/sub&gt;</td>
<td>WCl&lt;sub&gt;6&lt;/sub&gt;</td>
</tr>
<tr>
<td>WCl&lt;sub&gt;(g)&lt;/sub&gt;</td>
<td>W&lt;sub&gt;Clo&lt;/sub&gt;</td>
</tr>
<tr>
<td>WCl&lt;sub&gt;(g)&lt;/sub&gt;</td>
<td>WCl&lt;sub&gt;6&lt;/sub&gt;</td>
</tr>
<tr>
<td>W(CO)&lt;sub&gt;6&lt;/sub&gt;</td>
<td>WO&lt;sub&gt;2(OH)&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

NASA’s Chemical Equilibrium with Applications (CEA) software was selected for conducting the majority of the chemical equilibrium calculations of this study (McBride and Gordon 1996). Originally, this database was found to be missing several species shown in Table 4-1. The species shown in bold were added to the CEA database.

CEA calculates equilibrium mixtures by defining two thermodynamic states, such as temperature and pressure. These two states are used most often since they are the easiest states to define experimentally, however, other states such as enthalpy, specific volume, or entropy may be defined as well. CEA determines equilibrium compositions of complex mixtures by using the minimization of Gibbs free energy formulation (i.e., minimization of Helmholtz energy or maximization of entropy). Detailed discussion of the mathematical analysis used for this formulation may be found in the CEA manual (McBride and Gordon 1996).

Using CEA and the updated thermodynamic database, nearly any temperature and pressure of interest may be studied, determining the equilibrium tungsten reaction products. The tungsten surface may be modeled by assuming a large majority of the system to be tungsten, as would be the case in the near surface region of a rocket nozzle. The equated equilibrium species indicate possible reaction products, and therefore desorption species. Intermediates species may be estimated based on these calculations as well. For example, if WO<sub>3</sub> is determined to be the primary reaction product, and likely the prominent desorption
species, it follows that $WO_{(s)}$ and/or $WO_{2(s)}$, must be formed at some point during the reaction progression, and are therefore intermediate species. Intermediate and product species are also generated from bi-products of the oxidation reaction. For instance, $H_2O$ oxidizes tungsten forming $H_2$, which becomes a primary product species in the overall reaction if $H_2O$ is present in appreciable quantities.

Assuming local thermodynamic equilibrium and using programs such as CEA is just one means of predicting important species in a high temperature tungsten oxidation mechanism. As computer modeling and calculation speeds have increased over time, many new tools have become available to scientists and engineers for predictions of reaction mechanisms and important species. One of these tools is computational chemistry and physics utilizing density functional theory (DFT). DFT predicts the energetic ground states of many body systems (i.e., atoms and molecules). Using this theory the most energetically favorable reaction pathways of a reaction may be determined. An advantage of this theory is that it is a simple, yet powerful enough to model large multi-atom or molecule systems such as multi-layer surfaces. An example of such a calculation is shown in Fig. 4-1, which is a potential energy surface (PES) diagram of the reaction progress. This illustrates the predicted reaction pathway for the dissociative adsorption of a $H_2O$ molecule on a tungsten surface. The process shows the formation of $WO_{(s)}$ (i.e., $O_{(a)}$) surface species, and two loosely bound $H$ atoms. This is the initial oxidation step of the overall tungsten oxidation process. Adsorption of additional oxygen and migration of $O_{(a)}$ leads to further reactions, forming $WO_2$ and $WO_3$. DFT, in combination with chemical reactivity theories such as RRKM (Rice, Ramsperger, Kassel, and Marcus), allows for prediction of several kinetic parameters such as activation energies and pre-exponential factors used in the Arrhenius rate equation (Eq. 2-5). It is quite evident that these calculations provide invaluable information for the development of heterogeneous reaction mechanisms. As part of a joint research effort in studying nozzle corrosion mechanisms, a computational chemistry research group at Emory University in Atlanta, Georgia completed a series of investigations to increase understanding of tungsten oxidation reactions. At the time of this writing, they had published several papers on this subject which provide information regarding initial oxidation steps (Musaev et al. 2006; Chen et al. 2007a; Chen et al. 2007b; Musaev et al. 2007; Chen et al. 2008a; Chen et al. 2008b; Chen et al. 2009).
There are several caveats that come with the interpretation of these types of calculations. Due to the small scale at which these calculations are performed, they may not reflect reactions occurring at other sites on a bulk surface. In Chapter 2, surface defect sites were briefly discussed, and often these sites are the most reactive. In most DFT calculations such as the one above, pristine surfaces are considered, which are free of defects. Defects can have considerable effects on the surface energetics at the scale of these calculations. Consider the DFT calculation for the reaction given in Eq. 4-1 (Fig. 4-2). In this reaction, a single oxygen atom chemisorbs on to a pristine $W(111)$ surface, leading to the subsequent removal of $WO$, causing corrosion of the surface, and the formation of a defect site. Using known enthalpies of formation for the gas-phase species, and assuming a value of 0 kcal/mol for a pristine tungsten surface, an enthalpy of formation for the defected surface site is estimated to be -26 kcal/mol, which is a rather large variation from the pristine surface. If it
is assumed that removal of tungsten from a pristine surface affects several $W$-surface atoms, this chemical bonding may be shared, appreciably reducing the variation in the energetics estimated for a pristine and defective surface. This implies that energetics, and therefore reaction mechanisms may greatly transform depending on the morphology of the surface.

$$W_{(s),\text{pristine}} + O (+W_{(b)}) \leftrightarrow WO_{(s)} (+W_{(b)}) \rightarrow W_{(s),\text{defect}} + WO$$  \hspace{1cm} (4-1)

A second caveat is that computational chemistry is often limited by the level of knowledge and the creativity of the modeler. Computations of the type above do not consider states that are not provided by the modeler. Certain energetically favorable states and reactions may occur in the real reaction, but may not be considered in the computation. As in equilibrium calculations, where the exclusion of an unknown species may lead to inaccurate conclusions, DFT shares the same pitfalls if all possible states are not considered.

It is clear from the calculations shown in Fig. 4-1 and Fig. 4-2 that in the global tungsten oxidation (or corrosion) process, desorption of oxides have much greater energy barriers than the formation of oxides. This implies that desorption may be the rate limiting

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**Figure 4-2:** Schematic of the relative PES for the adsorption of $O$ on a $W(111)$ surface, and subsequent desorption of $WO$ using DFT, source: (Lin et al. 2010).
process, particularly at lower temperatures, however, frequency factors of desorption
processes may be high.

4.2 Numerical Modeling of the Flow Reactor

In order to learn details of the tungsten oxidation process and begin developing more
advanced kinetic mechanisms for modeling applications, the TG flow reactor experiment
used in this study was modeled numerically under the assumptions of an open, constant
pressure, temperature, and volume system. Also assumed were no spatial dependences,
which dictates that reactions are independent of surface coverage, and subsurface reactions
are assumed not to occur. In the case of high temperature tungsten oxidation, the bulk
material is removed continuously and may exist in the bulk, surface, and gas-phases
according to SURFACE CHEMKIN formalism (Coltrin et al. 1991). Since oxides are
removed continuously, no bulk-phase oxides were allowed to exist in this model. This model
was developed through the modification of an iron carburization flow reactor model (Wang
2007; Wang and Yetter 2009). Iron carburization is a high temperature heterogeneous
process between iron and a $C$-containing species that leads to increased carbon content in the
iron, altering its physical and chemical properties (Wang 2007). Unlike high temperature
tungsten oxidation where the bulk material is continually lost, in iron carburization bulk
material is continually added in the form of carbon.

A diagram of the modeled system is shown in Fig. 4-3. Reactive and inert carrier gas
mixtures were flowed in at a constant flow rate ($\dot{m}_{in}, \text{g/s}$) from left to right through a defined
volume ($V, \text{cm}^3$) and passed over a tungsten foil of defined surface area ($A, \text{cm}^2$). The mass
flow rate of the system was allowed to change within the control volume (CV) due to
reactive gas adsorption, or production of volatile tungsten species. The mass fraction of each
species $k$ within the CV was $Y_k$. 

4.2.1 Governing Equations

The following section presents the governing equations of the numerical flow reactor numerical model. These were separated based on the species phases: gas, solid, and surface. The assumptions of constant temperature and pressure greatly reduced the complexity of governing equations since only mass conservation equations of these phases were required.

The conservation of mass equations for each phase were predominately non-linear equations. Non-linear equations were solved by the CHEMKIN-III and SURFACE CHEMKIN-III software packages, which used a VODE (Variable-coefficient Ordinary Differential Equation) solver. More detailed information regarding this solver may be found in the program manual (Coltrin et al. 1996; Kee et al. 1996).

4.2.1.1 Gas-phase Species Mass Conservation

With the assumption of a constant pressure control volume, the number of gas-phase moles remained unchanged during the reaction process, therefore \( \frac{dn_i}{dt} = 0 \), where \( n_i \) is the total number of moles within the CV. It followed that the exit mass flow rate from the system was defined using Eq. 4-2, where \( MW_k \) is species \( k \)’s molecular weight, \( \dot{S}_k \) (mole/cm\(^2\)) is the molar production (or destruction) rate of gas-phase species \( k \) due to

\[ \text{Figure 4-3: Diagram of the open system flow reactor model.} \]
heterogeneous reactions, and \( \dot{\omega}_k \) (mole/cm\(^3\)) is the molar production (destruction) rate of gas-phase species due to homogeneous reactions. The overall system mass conservation equation is given by Eq. 4-3, where \( \rho \) (g/cm\(^3\)) is the gas-phase density. The conservation of mass of each individual species (gas-phase) is described by Eq. 4-4.

\[
\sum_{k=1}^{k_g} \left( \frac{\dot{m}_{in} \cdot Y_{in,k}}{MW_k} - \frac{\dot{m}_{out} \cdot Y_{out,k}}{MW_k} + A \cdot \dot{S}_k + V \cdot \dot{\omega}_k \right) = 0
\]  

\[
\frac{d\rho}{dt} = \frac{\dot{m}_{in}}{V} + \sum_{k=1}^{k_g} A \cdot \frac{MW_k \cdot \dot{S}_k}{V} - \frac{\dot{m}_{out}}{V}
\]  

\[
\frac{dY_k}{dt} = Y_k \frac{\dot{m}_{in}}{\rho V} - \frac{Y_k}{\rho} \frac{d\rho}{dt} + MW_k \frac{\dot{S}_k}{\rho V} + MW_k \frac{\dot{\omega}_k}{\rho V} - Y_k \frac{\dot{m}_{out}}{\rho V} \bigg|_{k=1,2,...,k_g}
\]

### 4.2.1.2 Surface-phase Species Mass Conservation

At the surface of the bulk material, the number of moles of species \( k \) (\( N_k \)) was correlated using Eq. 4-5, where \( Z_k(n) \) is the site fraction of surface sites (\( n \)) occupied by species \( k \), \( \Gamma_n \) (moles/cm\(^2\)) is the density of surface sites, and \( \sigma_k(n) \) is the number of sites each species \( k \) occupies. The rate at which surface-phase species \( k \) is generated (or destroyed) was described by Eq. 4-6, where \( k = k_f, k_{f+1},..., k_l \) and the subscripts \( f \) and \( l \) represent the first and last surface species, respectively. The surface coverage was described as a function of time by Eq. 4-7, where \( d\Gamma_n/dt \) is the rate of change of the surface site density, which was defined as zero in the numerical model since the surface area and the bulk material structure were assumed constant.

\[
N_k = Z_k(n) \cdot \Gamma_n \cdot \frac{A}{\sigma_k(n)}
\]

\[
\frac{dN_k}{dt} = A \cdot \dot{S}_k
\]
4.2.1.3 Solid-phase Species Mass Conservation

The molar destruction (or generation) rate of a bulk species \( k \) by surface reactions was correlated using Eq. 4-8, which is the same equation as with surface species. The bulk species destruction rate was coupled to the gas-phase reactions, in order for bulk material to be destroyed in this model, heterogeneous reactions must occur that transfer surface species into the gas-phase. No account was made in this model for loss of surface or bulk species due to physical factors such as oxide scale spalling or molten oxide removal. In the high temperature tungsten oxidation model it was assumed no species diffuse into the pure bulk material, therefore the only bulk species was tungsten. As with the surface species conservation, each bulk species was indexed accordingly \((k_{f,bulk} = k_{l,bulk} = W)\).

\[
\frac{dZ_k(n)}{dt} = \sigma_k(n) \frac{\dot{S}_k}{\Gamma_n} - \frac{Z_k(n)}{\Gamma_n} \frac{d\Gamma}{dt}
\]  

(4-7)

4.2.2 Model Operation and Validation

An outline of the numerical model’s structure is shown in Fig. 4-4. Two separate input files were prepared, which contain all elements, species, and kinetic data. One input file contains solely gas-phase data, the second contains surface and bulk phase data, including \( \sigma_k(n) \) and \( \Gamma_n \). Thermochemistry data of the various species may be contained within these input files, or within a database file that is shared by the CHEMKIN and SURFACE CHEMKIN utilities. A more detailed breakdown of the operation of the CHEMKIN utilities is shown in Fig. 4-5. As you can see, once the CHEMKIN interpreter was run, a linking file was created, which was used by the application program in conjunction with the CHEMKIN subroutine library to model chemical reactions occurring within the model’s CV. In the case of the SURFACE CHEMKIN utility, the gas-phase
linking file was used as an interpreter input, as well as the surface/bulk chemistry inputs. For this reason, the gas-phase utility must be run prior to running the surface/bulk phase utility.

**Figure 4-4: Flow chart of the numerical flow reactor model operation utilizing CHEMKIN and SURFACE CHEMKIN.**

The flow reactor inputs were $T$, $P$, $A$, $V$, incoming gas species and molar concentrations ($Y_i$), and initial surface-phase concentrations, in addition to model integration and run times. The surface site density, $\Gamma_n$ (moles/cm$^2$), was estimated by assuming a crystallographic surface. Using a $W(111)$ surface, which has been found experimentally to

**Figure 4-5: Flow chart of the CHEMKIN utility operation.**
have oxidation rates close to that of a polycrystalline surface (Bartlett and McCamont 1965), a surface site density of approximately $9.43 \times 10^{-10}$ moles/cm$^2$ was determined. This assumes on-top sites to be active sites (Chen et al. 2007b; Chen et al. 2008b), and a cubic edge length of 0.319 nm (Ross and Hume-Rothery 1963).

The flow reactor model was verified to be working correctly by considering several single-step reactions. These included molecular adsorption (Fig. 4-6), and desorption reactions (Fig. 4-7), as well as a dissociative adsorption reaction (Fig. 4-8). Two temperatures were considered for the desorption and dissociative adsorption reactions. In Fig. 4-7, the surface was initially considered to be completely covered by $WO_{2(s)}$, and the higher temperature situation creates a faster initial erosion rates, and therefore removes all oxygen from the surface quicker than it would at lower temperatures. The kinetics are the same in Fig. 4-8 since no activation energy was applied to the reaction mechanism, and therefore there is no temperature dependence. In all cases, analytical solutions matched that of the numeric model.

![Figure 4-6: Numerical model verification of molecular adsorption kinetics.](image)
Figure 4-7: Numerical model verification of desorption/corrosion kinetics.

Figure 4-8: Numerical model verification of dissociative adsorption kinetics: (a) 1750 K and (b) 2000 K.
4.2.3 Gas-phase Reaction Mechanisms

Gas-phase reactions occurring in the modeled flow reactor were solved using standard kinetic mechanisms using CHEMKIN-III (Kee et al. 1996). The homogeneous gas-phase mechanisms used came from Li et al. and included all standard combustion species, including all C, O, and H atom containing species needed to accurately solve for species concentrations as a function of time (Li et al. 2007). The original mechanism put together by Li et al. was significantly reduced, removing all nitrogen containing species, C-H species, and all H-O species generally associated with higher pressure reactions (i.e., HO₂ and H₂O₂). None of these species are expected to play an important role at the conditions considered in the TG flow reactor study. With these reductions, 13 reversible gas-phase reactions remained (Table 4-2). Homogeneous reactions involving tungsten containing species were not found in the literature. However, it is believed that these reactions can be neglected in the modeling of the TG reactor with reasonable accuracy, particularly due to the high flow rates used. Since concentrations of any gas-phase tungsten species were small compared to total system pressure, and TGA samples were continuously flushed, it is assumed any gas-phase reactions of the desorption products did not affect measured reaction rates appreciably.

All mechanisms are described in Table 4-2 using CHEMKIN formalism. Several of the reactions are three-body reactions, where ‘M’ indicates any third-body gas-phase species. In these cases, often enhanced third-body efficiencies (ε_i) are applied to various species i. Other three-body reactions are pressure dependent, as indicated in reaction 11 by (+M). This reaction is termed a unimolecular/recombination fall-off reaction. In this Lindeman type of reaction, the third body is required to carry away enough energy to cause recombination or contribute enough energy for dissociation. In these types of reactions there are two limiting-rate constants for the reaction, a low pressure limit that is temperature dependent (k₀), where the reaction is second order, and a high-pressure limit (k∞), where the reaction behaves as a unimolecular reaction. See Fig. 4-9 for a visual representation of the methyl recombination reaction. Details regarding the description and applied mathematics of these mechanisms may be found in the CHEMKIN-III manual (Kee et al. 1996).
Table 4-2: Reduced gas-phase reaction mechanism from Li et al. (Li et al. 2007).

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>$k_{forward} = A \cdot T^\beta \exp\left(-\frac{E}{R_T \cdot T}\right)$</th>
<th>A</th>
<th>$\beta$</th>
<th>$E$, cal/mol</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$H + O_2 \leftrightarrow O + OH$</td>
<td>$3.55E+15 \cdot T^{-0.4}$</td>
<td>3.55E+15</td>
<td>-0.4</td>
<td>16599</td>
<td>(Hessler 1998)</td>
</tr>
<tr>
<td>2</td>
<td>$O + H_2 \leftrightarrow H + OH$</td>
<td>$5.08E+04 \cdot T^{2.7}$</td>
<td>5.08E+04</td>
<td>2.7</td>
<td>6290</td>
<td>(Sutherland et al. 1986)</td>
</tr>
<tr>
<td>3</td>
<td>$H_2 + OH \leftrightarrow H_2O + H$</td>
<td>$2.16E+08 \cdot T^{1.5}$</td>
<td>2.16E+08</td>
<td>1.5</td>
<td>3430</td>
<td>(Michael and Sutherland 1988)</td>
</tr>
<tr>
<td>4</td>
<td>$O + H_2O \leftrightarrow OH + OH$</td>
<td>$2.97E+06 \cdot T^{2.0}$</td>
<td>2.97E+06</td>
<td>2.0</td>
<td>13400</td>
<td>(Sutherland et al. 1990)</td>
</tr>
<tr>
<td>5</td>
<td>$H_2 + M \leftrightarrow H + H + M$</td>
<td>$4.58E+19 \cdot T^{-1.4}$</td>
<td>4.58E+19</td>
<td>-1.4</td>
<td>104380</td>
<td>(Tsang and Hampson 1986)</td>
</tr>
<tr>
<td>6</td>
<td>$H_2 + He \leftrightarrow H + H + He$</td>
<td>$5.84E+18 \cdot T^{-1.1}$</td>
<td>5.84E+18</td>
<td>-1.1</td>
<td>104380</td>
<td>(Tsang and Hampson 1986)</td>
</tr>
<tr>
<td>7</td>
<td>$O + O + M \leftrightarrow O_2 + M$</td>
<td>$6.16E+15 \cdot T^{-0.5}$</td>
<td>6.16E+15</td>
<td>-0.5</td>
<td>0.0</td>
<td>(Tsang and Hampson 1986)</td>
</tr>
<tr>
<td>8</td>
<td>$O + O + He \leftrightarrow O_2 + He$</td>
<td>$1.89E+13 \cdot T^{0.0}$</td>
<td>1.89E+13</td>
<td>0.0</td>
<td>-1788</td>
<td>(Tsang and Hampson 1986)</td>
</tr>
<tr>
<td>9</td>
<td>$O + H + M \leftrightarrow OH + M$</td>
<td>$4.71E+18 \cdot T^{-1.0}$</td>
<td>4.71E+18</td>
<td>-1.0</td>
<td>0.0</td>
<td>(Tsang and Hampson 1986)</td>
</tr>
<tr>
<td>10</td>
<td>$H + OH + M \leftrightarrow H_2O + M$</td>
<td>$3.80E+22 \cdot T^{-2.0}$</td>
<td>3.80E+22</td>
<td>-2.0</td>
<td>0.0</td>
<td>(Li et al. 2004)</td>
</tr>
<tr>
<td>11</td>
<td>$CO + O(+M) \leftrightarrow CO_2 (+M)$</td>
<td>$k_r = 1.80E+10$ $\cdot T^{0.0}$</td>
<td>1.80E+10</td>
<td>0.0</td>
<td>2384</td>
<td>(Troe 1979)</td>
</tr>
<tr>
<td>12</td>
<td>$CO + O_2 \leftrightarrow CO_2 + O$</td>
<td>$2.53E+12 \cdot T^{0.0}$</td>
<td>2.53E+12</td>
<td>0.0</td>
<td>47700</td>
<td>(Tsang and Hampson 1986)</td>
</tr>
<tr>
<td>13</td>
<td>$CO + OH \leftrightarrow CO_2 + H$</td>
<td>$2.23E+05$ $\cdot T^{-1.9}$</td>
<td>2.23E+05</td>
<td>1.9</td>
<td>-1160</td>
<td>(Li et al. 2007)</td>
</tr>
</tbody>
</table>

![Figure 4-9: Fixed temperature rate constants as a function of pressure for the unimolecular fall-off reaction: $CH_3 + CH_3 (+M) \leftrightarrow C_2H_6 (+M)$, source: (Kee et al. 1996).](image-url)
4.2.4 Surface Reaction Mechanisms

The high temperature oxidation of tungsten was treated as solely a heterogeneous process. The surface was oxidized by various species, forming higher volatile oxides. Since homogenous reactions involving tungsten containing species were neglected, desorption species were assumed to be the products of the overall tungsten oxidation process and subsequent reactions did not occur.

The development of the surface reaction mechanism was the primary focus of this work. Using the tools outlined above, the appropriate species – reactants, intermediates, and products – were identified and reactions were postulated. The use of experimental studies and DFT can be very helpful in this process. Each reaction in the mechanism must be described using the modified form of the Arrhenius reaction rate expression (see Table 4-2) so that it may be interpreted by SURFACE-CHEMKIN III. The modified Arrhenius rate correlation provides temperature dependence to the pre-exponential component of the equation, which conforms to most theories. The most important factors of the Arrhenius expressions are the pre-exponential factor and the activation energy. These terms can be estimated using several theoretical means.

Quantum mechanics based DFT is the most powerful of these theories since these calculations may predict both structures and activation energies. DFT is well known, detailed discussions of DFT and its history are provided by several texts (Parr and Yang 1994; Cramer 2002). The level of detail, and required computing power of these calculations often limit the quantity of available data, requiring reaction mechanism development to rely on more simplified theories, which depend heavily on thermochemical knowledge of gas- and solid-phase species. These theories include transition state theory (TST) and bond energy theory.

In solid body collision theory, the reaction rate is a function of the collision rate between reactants, which are assumed to be solid bodies (surfaces, spheres, etc.). The reaction rate constant according to modified collision theory is defined by Eq. 4-9 for a reaction \( A + B \rightarrow C \), where \( Z_{AB} \) is the collision number or frequency (Eq. 4-10), \( p \) is the steric or probability factor, and \( E_a \) is the activation energy. In Eq. 4-10, \( d_{AB} \) is the mean molecular diameter (collision cross-section) assuming species \( A \) and \( B \) to be hard spheres, \( N_A \)
is Avogadro’s number, \( m_i \) is the mass of species \( i \), and \( k_B \) is Boltzmann’s constant. In the case of heterogeneous reactions, the steric factor may be termed the sticking probability, which is the probability that a gas-phase reactant striking the bulk reactant surface will react, instead of bouncing off the surface without reacting. The use of factors such as this illustrates our naïve understanding of heterogeneous, and homogeneous chemical reactions, as well as the difficulties in modeling them.

\[
k(T) = pZ_{AB} \cdot \exp\left( -\frac{E_a}{RT} \right)
\]  
\[
Z_{AB} = Na \cdot d_{AB}^2 \left( 8\pi k_B T \frac{m_A + m_B}{m_A m_B} \right)^{1/2}
\]

TST, also referred to as absolute reaction rate theory, or activated complex theory (ACT), is an extension of collision theory that can be used to determine pre-exponential factors of individual reactions. The ACT or TST were established based on the theory that a reaction occurring between two species must pass through an activated complex or transition state, which then dissociates into product species, or back into the reactants. This reaction, described by Eq. 4-11 is represented schematically by Fig. 4-10 for an endothermic \(( E_1 - E_2 > 0 )\) or exothermic reaction \(( E_1 - (E_2 + E_3) < 0 )\). In each reaction, an applied amount of energy equal or greater than \( E_1 \) is needed to initiate the reaction.

\[
A + B \xrightleftharpoons[\kappa_{-1}]{\kappa_1} AB \xrightarrow[k_2]{k_1} Products
\]

Under the assumptions of steady-state and \( k_2 << k_{-1} \), the rate of product formation may be determined by the concentrations of reactants, and a ratio of rate constants. Recognizing that equilibrium is reached between the activated complex and the reactant, the ratio of the forward to reverse rate constants may be expressed as a ratio of partition functions, based on statistical mechanics. With further manipulation and understanding of the partition functions, the rate of product formation may be expressed by Eq. 4-12, where \( q \) is the associated partition function of each species, and \( h \) is Planck’s constant. Further details of ACT and collision theory may be found in several sources (Laidler 1965; Houston 2006).
When collision theory is applied to surface reactions, several factors change. Adsorption of reactants is the first chemical step of a heterogeneous reaction. The adsorption rate \( \dot{r}_a \) may be written as Eq. 4-13, where \( \theta \) is the fraction of surface sites covered by adsorbates (i.e., \( 1 - \theta \) is the fraction of available adsorption sites) and \( \left( \dot{i}_{(g)} \right) \) is the concentration of gas-phase adsorbates (Laidler 1965; Masel 1996). In the case of dissociative adsorption, where the adsorbate splits into two separate species, the rate of adsorption is expressed as Eq. 4-14.

\[
k(T) = \frac{k_B T}{h} \frac{q^+}{q_A q_B} \exp\left(\frac{-E_a}{RT}\right)
\]  

(4-12)

Figure 4-10: Diagram of reaction progress using activated complex theory.

\[
\dot{r}_{a,molecular}(T) = k_a(T) \cdot (1 - \theta) \cdot \left( \dot{i}_{(g)} \right)
\]

(4-13)

\[
\dot{r}_{a,dissociative}(T) = k_a(T) \cdot (1 - \theta)^2 \cdot \left( \dot{i}_{(g)} \right)
\]

(4-14)

In the literature, sticking probabilities are often defined for adsorption reactions. Sticking coefficients are determined experimentally by relating observed adsorption rates to
theoretical maximum rates. As with steric factors used in homogeneous reactions, sticking probabilities must be less than unity and are often small values. In order for chemical kineticists to utilize this information in mass action kinetics, one can use Eq. 4-15 (Kee et al. 2003), where $\Gamma_{\text{tot}}$ is the total surface site concentration, and $\lambda$ is the sum of all of the surface reactants’ stoichiometric coefficients (i.e., the number of surface sites need for the adsorption reaction to occur). The denominator in the first term is required to convert the unitless sticking coefficient to units appropriate for a kinetic rate constant. The second term is the collision frequency between the adsorbate and the surface according to kinetic theory. The following equation was deemed valid only when the sticking coefficient is relatively small – much less than one (Kee et al. 2003).

$$k_{a,i}(T) = \frac{s_i}{(\Gamma_{\text{tot}})^{\lambda}} \sqrt{\frac{Ru \cdot T}{2\pi \cdot MW_i}}$$

(4-15)

At higher reactant concentrations and sticking coefficients, two corrections for Eq. 4-15 have been developed (Motz and Wise 1960; Dorsman and Kleijn 2007). The first correction by Motz and Wise was developed using theoretical means, and predicts rate constants for situations in which the sticking coefficient is large, but the concentrations of adsorbates must be very small (Eq. 4-16). In a more recent study, which used direct simulation Monte Carlo (DSMC), Dorsman and Kleijn developed an additional correction to Eq. 4-16, allowing for prediction of adsorption rates of species at very high concentrations and sticking coefficients. An additional dependence on the reactant mass fraction near the surface ($X_i^s$) was included (Eq. 4-17).

$$k_{a,i}(T) = \frac{s_i \left[ \frac{1}{1 - s_i/2} \right]}{(\Gamma_{\text{tot}})^{\lambda}} \sqrt{\frac{Ru \cdot T}{2\pi \cdot MW_i}}$$

(4-16)

$$k_{a,i}(T) = \frac{s_i \left[ \frac{1}{1 - s_i/2} \right] \left[ 1 + 0.19s_i^2 (1 + 0.84X_i^s) \right]}{(\Gamma_{\text{tot}})^{\lambda}} \sqrt{\frac{Ru \cdot T}{2\pi \cdot MW_i}}$$

(4-17)
Desorption, like adsorption, is a very important step in a complete heterogeneous reaction. The desorption reactions considered may be first or second order, in both cases they may be described using the Arrhenius expression. Pre-exponential factors are approximated based on TST; for first order desorption, the transition state frequency factor \((A_d)\) can be approximated by Eq. 4-18, with the second bracketed term assumed to be unity.

\[
A_d = \left( \frac{k_B T}{\hbar} \right) \left( \frac{F_z}{F_A F_B C} \right) \approx \left( \frac{k_B T}{\hbar} \right) = 2.08 \times 10^{10} \cdot T 
\]  (4-18)

Activation energies may be estimated based upon reaction enthalpies, which are determined by requiring that \(H_a + H_d = H_r\), where the subscripts \(a\), \(d\), and \(r\) stand for the adsorption, desorption, and reaction enthalpies, respectively. The enthalpy of an adsorbed species on a tungsten surface may be estimated using Eq. 4-19, where \(WX_{(s)}\) is the adsorbed species and \(WX_{(g)}\) is the gas-phase equivalent species. This equation is based on the assumption that the gas-phase species bond energy is equivalent to the bond energy of a surface species of the identical chemical composition. Thermochemical data may not exist for some gas-phase species of interest, in these cases appropriate bond energies may be used for estimation. As the field of computational chemistry advances and ages, many of these parameters will be estimated, and may be found in literature.

\[
\Delta H_{f,T} \left( WX_{(s)} \right) = \Delta H_{f,T} \left( WX_{(g)} \right) - \left[ \Delta H_{f,T} \left( W_{(g)} \right) - \Delta H_{f,T} \left( W_{(b)} \right) \right] 
\]  (4-19)
Chapter 5

EXPERIMENTALLY DERIVED OXIDATION RATES

This chapter presents and discusses the experimental results of this dissertation involving the high temperature oxidation of tungsten. The chapter begins with an in depth experimental study of the oxidation rates involving various oxidizing gases. The objectives of these analyses are to help identify important steps in reaction mechanism and quantify global kinetic rates, which were used in cooperation with a comprehensive 1-D numerical model to develop a kinetic reaction mechanism. Since the primary motivation of this work was to develop a reaction mechanism to predict corrosion rates of rocket motor nozzles, this chapter concludes with a discussion of the predicted nozzle throat recession rates using the kinetic correlations derived in this study.

5.1 Thermogravimetric (TG) Analysis of Oxidation Rates

Using the TG analyzer (TGA), the bulk oxidation rates of tungsten have been studied up to 1700°C in gas-phase atmospheres of \(O_2\), \(CO_2\), and \(H_2O\). Effects of non-oxidizing species such as \(CO\), \(H_2\), and \(N_2\) were explored, as well as mixtures of \(CO_2\) and \(H_2O\). All testing was performed at an overall system pressure of 1 atm using helium as a carrier gas.

5.1.1 Oxidation by Molecular Oxygen

The oxidation rate of bulk tungsten in the presence of molecular oxygen was studied at partial pressures between 0.152 and 3.8 torr (0.02 – 0.51 kPa or 0.0002 – 0.005 atm). The overall oxidation rates were found to be very fast. Therefore, at the highest temperatures considered, diffusion limited reactions were found, as indicated by the onset of what appears to be inversely temperature dependent kinetics at high temperatures in Fig. 5-1. The rates
decrease with increasing temperature in the diffusion limited region due to decreasing Reynolds numbers (see Appendix C). A maximum reactor flow rate of 17 slpm was used in this study; larger flow rates were not used due to concerns of reducing the reactor temperature. In order to determine the activation energy of the tungsten and oxygen heterogeneous reaction ($E_{a_{W-O_2}}$), the highest temperatures were neglected (>1800 K) determining the activation energy to be 22.6 kcal/mol on average, with a standard deviation of 1.4. This activation energy is within the range of values found by previous researchers (14.3 – 48 kcal/mol), as shown in Table 2-6. However, many of these studies involved either lower temperatures or static flow conditions. The work by Walsh et al. is the only study in which high flows were used to remove diffusion limited reactions at very high temperatures (Walsh et al. 1967a), determining $E_{a_{W-O_2}}$ to be 23 kcal/mol, nearly the exact value determined in this study.

![Figure 5-1: Isothermal tungsten consumption rates in presence of O₂ (lines from Eq. 5-1).](image-url)
The oxidation rate dependence on the $O_2$ partial pressure was determined from the slope of constant temperature data when plotting $\ln(\dot{n}_{W-O_2})$ verse $\ln(P_{O_2})$, as explained in 3.1.5, determining the pressure exponent ($n_{W-O_2}$) to be 0.90 with a standard deviation of 0.01 (Fig. 5-2). Tests which determined this pressure exponent were conducted in the same session, using the same sample, minimizing errors and uncertainties. The $O_2$ partial pressures used ranged from 0.152 to 3.8 torr during these tests. The pressure exponent of near unity indicates a reaction rate proportional to the collision frequency of $O_2$ molecules with the bulk surface. Other researchers have found pressure exponents as high as 1.35 (Harvey 1973) and as low as 0.55 (Bartlett 1964). Much of the previous literature does not report a pressure exponent.

![Figure 5-2: $O_2$ pressure dependence of tungsten oxidation reaction.](image)

Using the pressure dependence of the $W-O_2$ oxidation reaction derived above, the Arrhenius reaction rate pre-exponential factor ($A_{W-O_2}$) was estimated using the procedures presented in 3.1.5. The plot of these data showed that nearly all the data are within ±20% of
the experimental curve fit to these data (see Fig. 5-3). These results provide an initial estimate of an appropriate analytical model of tungsten oxidation by \(O_2\); however, the model was refined within the range of uncertainty, increasing accuracy of the correlation with the majority of the data. This model is expressed in Eq. 5-1, and illustrated in Fig. 5-1, where the molecular weight of tungsten is 183.84 g/mol. The derived Arrhenius rate correlation predicts measured rates within acceptable limits of error.

\[
\dot{n}_{W-O_2} = A_{W-O_2} \cdot \exp \left( \frac{-E_{W-O_2}}{R \cdot T_s} \right) \cdot (P_{O_2})^{n_{W-O_2}} \\
= 6.99 \times 10^{-2} \frac{\text{grams of } W}{\text{cm}^2 \cdot \text{sec} \cdot \text{torr}^{0.89}} \cdot \exp \left( \frac{-23.5 \text{ kcal/mol}}{R \cdot T_s} \right) \cdot (P_{O_2})^{0.89}
\]  

(5-1)

Figure 5-3: Arrhenius reaction rate pre-exponential factor estimation for the tungsten and \(O_2\) oxidation reaction.
In order to compare various correlations, empirical models developed in this dissertation and by previous researchers were used to predict data from Walsh et al. at a single \(O_2\) partial pressure (Fig. 5-4). As stated by Walsh et al., the data from Perkins et al. (Perkins et al. 1962) matches the data from Walsh et al. at high temperatures. The correlation developed in this study matches the trends of Walsh et al. well, however, the model developed here under-predicts their data considerably (i.e., about a factor of 4-5). However, the model represented in Eq. 5-1 comes closer to the model from Walsh et al. and Perkins et al. than the other models developed. All other studies were conducted at sub-atmospheric pressures. A definitive conclusion as the cause for the discrepancy between the data from this study and Walsh et al. was not realized. However, it should be noted that these experiments are fundamentally different in several areas. Walsh et al. used an inductively heated sample – gases are only heated by hot tungsten sample – in a stagnation flow reactor (Graff and Walsh 1967). Kinetics, temperature, and oxidizer partial pressure were calculated using pyrometry, pre- and post test measurement of stagnation point.
recession, and calculated oxidizer stagnation pressures, respectively. These all provide different levels of error than the current study, and in most cases levels of uncertainty are greater in the study by Walsh et al.

5.1.2 Oxidation by Carbon Dioxide

The oxidation rate of bulk tungsten in the presence of carbon dioxide was studied at partial pressures between 7.6 and 64.6 torr (1.01 – 8.61 kPa or 0.01 – 0.085 atm). The overall oxidation rates were found to be slower than with $O_2$, and therefore overall reactor flow rates of 7 slpm were found to produce kinetically limited reaction rates at all temperatures considered. Oxidation rate results at various $CO_2$ partial pressures are shown in Fig. 5-5 as a function of temperature. Fitting the results of this figure to the Arrhenius expression (Eq. 3-2), the activation energy ($E_{a_{W-CO_2}}$) of the $W-CO_2$ reaction is determined to be on average 63.4 kcal/mol of reacted tungsten, with a standard deviation of 2.6 kcal/mol. This activation energy is nearly triple that of the $O_2$ oxidation reaction, indicating a much greater energy barrier in forming a gas-phase tungsten oxide from $CO_2$. This activation energy is lower than 79 kcal/mol, which is the value found by Walsh et al. (Walsh et al. 1967b). A summary of the previous reaction kinetics studies of $W$ and $CO_2$ is shown in Table 2-9.
The dependence of the oxidation rate on CO$_2$ pressure was ascertained using the same procedure as with the W-O$_2$ system, determining the pressure exponent ($n_{W-CO_2}$) to be 0.60 with a standard deviation of 0.03 (Fig. 5-6). The pressure dependence, which is less than unity and close to 0.5, indicates a desorption or dissociation limited reaction. The limiting dissociation process could be due to the dissociative adsorption of CO$_2$ into CO$_{(g \text{ or } s)}$ and O$_{(s)}$. A limiting desorption process may be due to the CO$_{(s)}$ bi-product formed at the surface, or a volatile tungsten oxide. Detailed modeling is required in order to resolve dominant or limiting reaction routes. Using the pressure dependence of the W-CO$_2$ oxidation reaction, the Arrhenius reaction pre-exponential factor ($A_{W-CO_2}$) was estimated using the same graphical plotting procedure discussed previously. As with the previous system, these results provided an initial estimate of an appropriate analytical model of tungsten oxidation by CO$_2$. With refinement, an empirically derived kinetic model for tungsten oxidation by CO$_2$ was created, shown in Eq. 5-2. Most of the data were within ±15% of the Arrhenius fit, and nearly all data were within ±20%.
Although carbon monoxide was found to produce no measurable oxidation rates using the TGA, CO was found to affect oxidation rates of CO\textsubscript{2} considerably. This effect was previously observed by two groups of researchers (Olcott and Batchelor 1964; Walsh \textit{et al.} 1967b); however, Walsh \textit{et al.} was the only research group to quantify the effect of CO on the oxidation rates of CO\textsubscript{2} and W as a function of temperature and pressure. In this study, the

\begin{equation}
\dot{W} - \text{CO}_2 = A_{W - \text{CO}_2} \cdot \exp\left(\frac{-E_{a_{W - \text{CO}_2}}}{R u \cdot T_s}\right) \cdot (P_{\text{CO}_2})^{n_{W - \text{CO}_2}}
\end{equation}

\begin{equation}
= 2.54 \frac{\text{grams of } W}{\text{cm}^2 \cdot \text{s} \cdot \text{torr}^{n_{W - \text{CO}_2}}} \cdot \exp\left(\frac{-64 \text{ kcal mol}^{-1}}{R u \cdot T_s}\right) \cdot (P_{\text{CO}_2})^{0.6}
\end{equation}

5.1.2.1 Carbon Monoxide Inhibition

Although carbon monoxide was found to produce no measurable oxidation rates using the TGA, CO was found to affect oxidation rates of CO\textsubscript{2} considerably. This effect was previously observed by two groups of researchers (Olcott and Batchelor 1964; Walsh \textit{et al.} 1967b); however, Walsh \textit{et al.} was the only research group to quantify the effect of CO on the oxidation rates of CO\textsubscript{2} and W as a function of temperature and pressure. In this study, the
effects of CO addition on CO$_2$ oxidation rates were determined at a constant CO$_2$ partial pressure of 34.2 torr, and CO to CO$_2$ ratios up to 4 (Fig. 5-7). The activation energy of the W-CO$_2$ reaction was affected by the addition of CO as well. Curve fitting of the data in Fig. 5-7 illustrated activation energies of 59.1, 63.5, 65.7, 63.3, 70.7, 71.1, and 85.1 kcal/mol over a range of ratios from 0 to 4 in ascending order, indicating stronger temperature dependence when a large amount of CO is present. Up to a CO to CO$_2$ ratio of unity, activation energies are within experimental error of each other, signifying that the CO does not change the primary limiting reaction steps in the overall mechanism. However, at high ratios it seems clear that CO alters the limiting reaction steps.

![Figure 5-7: Effect of CO on the CO$_2$ oxidation rates of tungsten (dashed lines from Eq. 5-3).](image)

To better quantify the effect of CO on the rates of oxidation involving CO$_2$ and W, Fig. 5-8 was created and an empirical correlation was applied to the data (Eq. 5-3). The correlation performs well up to a CO to CO$_2$ ratio of 3. The results indicate that reaction rates are significantly affected by CO, even at ratios less than 0.33. These figures illustrate a temperature dependent pattern related to the CO addition. As a caveat, this correlation is a
greatly simplified approach for describing the presence of CO on the overall reaction rates, and therefore contains a great deal of empiricism.

The correlations perform well over the range of conditions in this study. Walsh et al. developed a similar equation; however, in their correlation the effect of CO is magnified with increasing temperature (Walsh et al. 1967b). Using the correlation from Walsh et al. (Eq. 2-16), the experimentally derived reaction rates of this study are under-predicted, but the greater activation energy and pressure dependence causes Eq. 5-3 to under-predict the experimental data presented by Walsh et al. If the correlation to correct for CO and CO₂

\[
\hat{W}_{\text{total,CO₂}} = \hat{W}_{\text{total,CO}} \times \exp\left[ -\left(2.194 \times 10^{11} \right) \left(\frac{P_{\text{CO}}}{P_{\text{CO₂}}}\right)^{3.574} \right] \\
= \frac{2.54 \text{ grams of } W}{\text{cm}^2 \cdot \text{wt in run}^2} \times \exp\left[ -\left(\frac{64 \text{ kcal mol}^{-1}}{R \cdot T_s} \right) \left(\frac{P_{\text{CO}}}{P_{\text{CO₂}}}\right)^{0.6} \times \exp\left[ -\left(2.194 \times 10^{11} \right) \left(\frac{P_{\text{CO}}}{P_{\text{CO₂}}}\right)^{3.574} \right] \right]
\]

(5-3)

Figure 5-8: Reduction in tungsten oxidation rate by CO₂ as function of the CO to CO₂ ratio.
mixtures developed by Walsh et al. is applied to Eq. 5-2, the reaction rates found in this study are over-predicted, as the calculated results indicate a \( CO_2 \) reaction rate reduction of less than 28% at the highest temperature (1973 K) and \( CO \) concentration (\( CO/CO_2 = 4 \)) studied, compared to a 77% reduction in this study. In addition to studying two different temperatures ranges, two significantly different experimental apparatuses were used in these studies, as described in 5.1.1. Additionally, total system pressures in the tests by Walsh et al. were less than 1 atmosphere. A comparison between the two correlations is illustrated in Fig. 5-9 at a single \( CO_2 \) partial pressure of 57 torr, with varying levels of \( CO \) addition. The greater activation energy and reduced effect of \( CO \) at lower temperatures are clearly shown.

![Figure 5-9: Comparison of empirical models for W-CO2 oxidation rates.](image)

The reduction in tungsten oxidation rates by \( CO_2 \) with the introduction of \( CO \) may be caused by several mechanisms. The first is a function of the experimental conditions. At very high temperature, \( CO_2 \) will dissociate, creating a mixture of \( CO, O \) and \( O_2 \).
addition of CO into a mixture of CO₂ will reduce the levels of dissociation at equilibrium. Using CHEMKIN 4.0 (Kee et al. 2004), the dissociation kinetics were modeled to determine how fast CO₂ dissociates under experimental conditions. The results showed that CO₂ will indeed dissociate, forming O₂ and O, which would increase reaction rates found using the TGA. At the highest temperatures considered, equilibrium concentrations of O₂ and O would cause severe increases in oxidation rates. However, negligible dissociation occurs at temperatures below 1400 K – determined using NASA’s CEA (Chemical Equilibrium with Applications) software (McBride and Gordon 1996) – and kinetics indicate that equilibrium conditions cannot be met given the time interval for dissociation of the CO₂ within the furnace prior to reaching the test sample. Time intervals of no greater than 50 – 150 ms were estimated, given a constant flow rate (7 slpm) and varying reactor temperatures. In fact, calculations would indicate that changes in CO₂ reaction rates due to O₂ formation were less than 10% at 2000 K and 0.5% at 1750 K with no CO addition (Fig. 5-10). When there is twice as much CO in the system than CO₂, changes are less than 0.5% at 2000 K. This variation is deemed acceptable given uncertainty in kinetic data. This analysis also verifies that the presence of CO directly affects the CO₂ oxidation rate. Additionally, experimental results indicate a stronger CO influence at lower temperatures, supporting the conclusion that CO₂ dissociation may not explain the reaction rate reduction. Moreover, if the dissociation of CO₂ were playing a significant role, reaction rates would increase dramatically at the highest temperatures studied when no CO is present. This result indicates that although dissociation of reactive gases should be considered in any experimental apparatus measuring reaction rates, it does not significantly affect CO₂ reaction rates found here, particularly at lower temperature, or in cases where CO is added to the gas mixture.
Another explanation for the reduction in reaction rates with CO addition are reduced concentrations of available adsorption or dissociation sites for CO₂, essentially poisoning the reaction by reducing available surface area, or reduction of surface oxides. Figure 5-11 helps explain this point, illustrating several simplified reactions. In each reaction, as the CO partial pressure increases, the reactions are driven in direction of reduced CO partial pressures. This can either reduce reactive surface sites through CO adsorption (‘a’), or reduce the tungsten oxides at the surface (‘b’ and ‘c’), each in turn reduces rates of tungsten surface atom volatilization. This shift in equilibrium of the global process \( W + 3CO_2 \leftrightarrow WO_3 + 3CO \) has been used in the past as the primary explanation for reductions in the CO₂ oxidation rates with CO addition (Olcott and Batchelor 1964).

Figure 5-10: Influence of CO on the dissociation of CO₂ and subsequent reaction with tungsten.
Based on the results of a recent theoretical study conducted by Chen et al. involving the adsorption of $CO_2$ and $CO$ on a $W(111)$ surface, a likely scenario occurring is that dissociative adsorption of both $CO_2$ and $CO$ poisons the surface oxidation process (Chen et al. 2008b), see process ‘a’. The $W-C$ bonding at the surface is calculated to be stronger than all other bonds at the surface (i.e., $W-CO_2$, $W-CO$, $W-O$) and highly resistant to desorption or surface diffusion processes. Therefore, the additional carbon present at the surface due to dissociative adsorption of $CO$ effectively reduces the available surface area for oxidation. The study of Chen et al. also estimated the kinetics of the adsorption processes. The dissociative adsorption rate of $CO$ is predicted to be approximately two orders of magnitude slower than $CO_2$ adsorption, however, this does not account for desorption processes. Although the initial process of $CO_2$ adsorption may occur faster, equilibrium surface concentrations of carbon atoms at the surface should quickly be approached. The results of Chen’s study are supported by other studies involving $CO$ adsorption on $W(111)$ surfaces (Hwu et al. 2001; Chen et al. 2006). These studies indicate that $CO$ oxidation is a self-poisoning process, as the $W-C$ bonding restricts dissociative adsorption of $CO$, thereby limiting the extent of oxidation, and not allowing higher tungsten oxides to form which could dissociate, leading to corrosion or mass loss of the tungsten substrate. The kinetics predicted by Chen et al. also indicated minimal activation energies for adsorption reactions. When compared to the global oxidation reaction energies found in the current study, these theoretical studies indicate that surface reactions or desorption processes are rate limiting.
Work involving mass-spectroscopic (MS) studies by Schissel and Trulson, presented in 2.2.1.1 would seem to contradict the possibility of CO blocking surface sites and inhibiting reactions (Aspinall 1965). In this unpublished study, significant amounts of CO were added to O2. Rates of tungsten oxide desorption were not altered by the presence of the CO in the MS study. The exact inhibiting mechanism is complicated by these conflicting results, further experimental and theoretical studies are require to resolve these issues.

5.1.3 Oxidation by Water Vapor

The oxidation rate of bulk tungsten in the presence of water vapor was studied at partial pressures between 3.04 and 51.3 torr (0.405 – 6.84 kPa or 0.004 – 0.0675 atm). Much of the data were collected at a H2O to H2 partial pressure ratio of 5 to ensure no O2 was left over from the steam generation process (see 3.1.2.1). The overall oxidation rates were found to be slower than with O2, but faster than CO2. System flow rates of 12 slpm were used for all tests involving H2O; at this flow rate kinetically limited oxidation rates are found (see 3.1.4). As with the other oxidizers, several previous experimental studies have considered the kinetics of the H2O and tungsten reaction, the most pertinent to this dissertation are presented in Table 2-6. A deficiency of many of the works discussed in Chapter 2 was that the steam pressure effects were not considered. For this reason a pressure exponent of unity was assumed for all correlations developed that do not provide a pressure exponent. In an unpublished study completed at the Union Carbide Research Institute, the effects of various partial pressures of steam were considered, although at lower pressures (Aspinall 1965). The Union Carbide researchers found diffusion limited reactions at the highest temperatures studied; however, at lower temperatures they indicated that an apparent activation energy of 60 kcal/mol was found, with a pressure exponent of 0.9. No correlation was developed by the Union Carbide researchers; therefore, their data was used to develop a correlation for comparison with other results (Eq. 5-4). Only lower temperature (< ~2020°C) data were considered, which were accepted to be kinetically or very nearly kinetically limited data. Using their data, the activation energy and pressure exponent were found to be 48.0 ± 5.5 kcal/mol and 0.80 ± 0.07, respectively. The frequency factor was fit to their data.
A common thread that appears in all the correlations from previous researchers is the temperature dependence of the reaction. In all but the high temperature data of Kilpatrick and Lott (see Eq. 2-19), which is believed to be diffusion limited, $E_{d_{W-H_2O}}$ is approximately 48 kcal/mol, which is in between the commonly found values for tungsten oxidation reactions involving $O_2$ and $CO_2$ oxidizers. Results from the current study are shown in Fig. 5-12 and Fig. 5-13. Using the data in Fig. 5-12, the $H_2O$ pressure exponent ($n_{W-H_2O}$) for the tungsten oxidation reaction was determined to be an average of 0.82 with a standard deviation of 0.05, which is well within the accepted limits of error of the correlation developed from the Union Carbide data. From Fig. 5-13, the apparent activation energy was determined to be 50.1 kcal/mol with a standard deviation of 1.4. 

This value for the activation energy matches closely with the correlations developed by previous researchers, although it is slightly greater. Temperatures as low as 1100°C were considered, finding that mass loss of
the tungsten foil occurred, however, the slow rates and noise in the data limited subsequent testing to temperatures greater than 1250°C.

Using the experimental data, an Arrhenius correlation for the global $W$-$H_2O$ reaction ($H_2 / H_2O = 0.2$) was developed with units of grams of $W$ per cm$^2$-sec (Eq. 5-5). It is recognized that the different correlations from previous researchers match fairly well with that of the equation below, although the predicted kinetic rates under most conditions are less than the previously developed correlations. However, it should be acknowledged that the rates of this study are somewhat inhibited by the presence of $H_2$.

$$
\dot{r}_{W-H_2O,H_2} = 5.307 \frac{\text{grams of } W}{\text{cm}^2 \cdot \text{s} \cdot \text{torr}^{0.82}} \cdot \exp \left( \frac{-50.1 \text{ kcal/mol}}{R \cdot T} \right) \cdot \left( P_{H_2O} \right)^{0.82}
$$  

(Eq. 5-5)
5.1.3.1 Hydrogen Inhibition

From the work of previous researchers (Hamamura 1959b; Olcott and Batchelor 1964; Andrievskii et al. 1981), as well as from initial testing of the steam generator used in cooperation with the TGA (Fig. 3-6), it is known that $H_2$ may significantly inhibit the oxidation rate of tungsten in the presence of $H_2O$. In order to quantify this effect and correct Eq. 5-5 for the presence of $H_2$, a series of tests were conducted over a temperature range of 1250 – 1695°C, and a $H_2$ to $H_2O$ ratio of 0.1 to 2. The temperature dependence of the tungsten oxidation kinetics at constant $H_2O$ partial pressure (15.2, 25.84, and 38 torr), and various ratios of $H_2$ addition are illustrated in Fig. 5-14. The plots show that $H_2$ significantly reduces tungsten mass loss rates. The apparent activation energy of the reaction is slightly reduced by the presence of $H_2$ as well, indicating that the inhibiting effects of $H_2$ are greater at higher temperatures. These results are contrary to what was found with $CO_2$ and $CO$, where the inhibiting effects of $CO$ were stronger at lower temperatures, producing greater apparent activation energies with increasing $CO$ concentrations.

In the same manner as with $CO$ and $CO_2$ mixtures, $H_2$ can reduce homogeneous dissociation of $H_2O$ (Fig. 5-15). Dissociation of gas-phase $H_2O$ creates larger concentrations of $O_2$, $O$, and $OH$, all of which are known oxidizers, and are either known – $O_2$ and $O$ – or anticipated to be better oxidizers than water. This effect was taken into account as a plausible explanation for the reduced oxidation rates of with $H_2$ presence; however, using the derived reaction rate kinetics of Eq. 5-1 and Eq. 5-6, this effect was deemed negligible under the conditions run ($H_2 / H_2O \geq 0.1$) in nearly all tests. From Fig. 5-16, it is shown that at the highest temperatures tested, using a $H_2$ to $H_2O$ ratio of 0.05, the effect of $O_2$ was less than 2%. Effects decrease even further with higher ratios. Though the effect of $OH$, whose concentration was least affected by $H_2$ addition, was not considered since it was unknown, it was believed that $O_2$ and $O$ are more reactive, or as reactive as $OH$. 
Figure 5-14: Effect of $H_2$ on tungsten oxidation rates at constant $H_2O$ partial pressures of: (a) 15.2, (b) 25.84, and (c) 38 torr (dashed lines generated using Eq. 5-6).
Although the exact mechanism(s) that cause $H_2$ to inhibit vaporization (i.e., corrosion) rates between tungsten and $H_2O$ is not fully understood at this time, it is known that most diatomic molecules adsorb dissociatively onto transition metal surfaces such as

![Figure 5-15: Effect of $H_2$ on the dissociation of $H_2O$ into smaller oxidizing species.](image1)

![Figure 5-16: Predicted $O_2$ oxidation rates formed through $H_2O$ dissociation.](image2)
tungsten, particularly at high temperatures (Masel 1996). Theoretical quantum chemical calculations using density functional theory (DFT) have indicated that \( WH(s) \) and \( WOH(s) \) are more energetically favorable than gas-phase \( H_2 \) and \( H_2O \) (Chen et al. 2007b). These theoretical results, along with the results from this study indicate that the \( H_2 \) is inhibiting the reaction rates in much the same way that \( CO \) inhibited the \( CO_2 \) reaction (see Fig. 5-11 and Fig. 5-17). Hydrogen may dissociatively adsorb on the surface (‘a’ and ‘b’), blocking sites and restricting oxidation and the formation of \( WO_{2(s)} \) or \( WO_{3(s)} \), which are precursor species to the formation of gas-phase \( W \)-oxides (\( i.e. \), erosion). The hydrogen may also reduce \( WO_{2(s)} \) or \( WO_{3(s)} \) (‘c’ and ‘d’) before tungsten oxides desorb from the surface. There are some indications that reaction ‘a’ may not be important at high temperatures, as an earlier study indicated that adsorption of hydrogen onto a clean tungsten surface is reduced with increasing temperature (Tamm and Schmidt 1971); similar results have been found with \( CO \) as well (Bowker and King 1980). These inhibition processes further cloud our understanding of the mechanisms involving tungstic acid formation, and the role it plays in the global oxidation process. It should be noted that Fig. 5-17 provides only a few examples of possible reaction processes, and may not represent all processes occurring in a real system.

![Figure 5-17: Reactions between \( H_2 \) and tungsten surfaces (both clean and oxidized).](image-url)
Using the data from Fig. 5-14, as well as the data presented in Fig. 5-18, it was found that the oxidation rates decay exponentially with $H_2$ addition. This rate of decay was also determined to increase with increasing temperatures, as indicated by the reduced apparent activation energies of reaction (Fig. 5-14). Using the experimentally obtained data, a correlation was developed to predict the mass loss rates of tungsten over the range of conditions studied (see Eq. 5-6). This empirical relation, which has a slightly greater $E_{aw-H_2O}$ compared to Eq. 5-5 due to the calculated effect of $H_2$, is presented graphically in many of the figures for comparison with experimentally derived rates. Although this correlation was developed purely by fitting the data to a mathematical representation using

**Figure 5-18: Exponential decay of $W-H_2O$ oxidation rates with increasing $H_2$ concentrations; $H_2O$ partial pressures of: (a) 7.6, (b) 15.2, and (c) 30.4 torr (dashed lines from Eq. 5-6).**
variables of temperature and partial pressures of $H_2O$ and $H_2$, providing slight insights into the detailed reaction mechanism, it does demonstrate the inhibiting effects of $H_2$, which are slightly temperature dependent. Agreement between the experimental data and Eq. 5-6 is illustrated to be good, particularly when there is less than a $H_2$ and $H_2O$ ratio of unity (see Fig. 5-13, Fig. 5-14, and Fig. 5-18). At higher concentrations of $H_2$ there tends to be more scatter in the data, and thus greater uncertainties.

$$
\dot{r}_{W-H_2O,H_2} = 9.29 \text{ grams of } W \text{ cm}^{-2} \text{ s}^{-1} \text{ torr}^{0.82} \exp \left( \frac{-50.9 \text{ kcal mol}^{-1}}{R \text{H} \cdot T} \right) \left( \frac{P_{H_2O}}{P_{H_2}} \right)^{0.82} 
\times \exp \left[ (6.86 - 1.14 \cdot \ln T) \left( \frac{P_{H_2}}{P_{H_2O}} \right) \right]
$$

(5-6)

Figure 5-19 compares the correlation developed in this study with those of previous studies. The correlations from previous studies were modified to account for the partial pressure of $H_2O$ and presented in Table 5-1. Each correlation was extrapolated well beyond the temperatures in which they were originally derived in order to reflect current and future rocket motor temperatures. The kinetically limited (i.e., low temperature) correlation from Kilpatrick and Lott is used in Fig. 5-19. For comparison, predicted rates for $W-CO_2$ (Eq. 5-2) and $W-O_2$ (Eq. 5-1) reactions are also shown. At both of the $H_2O$ partial pressures considered, the rates from all correlations are within one order of magnitude of each other, with the greatest rates predicted by the correlation from Unal et al. (Unal et al. 2000), and the lowest rates coming from the correlation of the current study or from Greene and Finfrock (Greene and Finfrock 2001), implying that Eq. 5-6 would produce a more conservative estimate of high temperature bulk tungsten corrosion rates.

When we compare the oxidation rates of $O_2$, $CO_2$, and $H_2O$ at a constant oxidizer partial pressures, the effects of the activation energies are shown. At most temperatures the $O_2$ reaction is by far the fastest, and the $CO_2$ reaction is the slowest. At very high temperatures it is possible that the $H_2O$ and $CO_2$ reaction rates could be on par with $O_2$. This is because the $O_2$ reaction has a relatively low activation energy, and the $CO_2$ reaction has a high activation energy, giving it a strong temperature dependence.
Figure 5-19: Kinetic correlation comparison for the $W-H_2O$ reaction ($H_2O$ partial pressures of 7.6 and 760 torr).

Table 5-1: Kinetic correlations for the $H_2O$ and tungsten reaction.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Kinetic Correlation, $\dot{r}_{W-H_2O}$ [grams of $W$ / (cm$^2$-sec)]</th>
<th>Temperature Range [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Kilpatrick and Lott 1966)</td>
<td>$6.81 \cdot \exp\left(-\frac{48.9 \text{ kcal mol}^{-1}}{R_u \cdot T}\right) \left(P_{H_2O,\text{torr}}\right)$</td>
<td>1323 – 1723</td>
</tr>
<tr>
<td></td>
<td>$1.14 \times 10^{-3} \cdot \exp\left(-\frac{22.7 \text{ kcal mol}^{-1}}{R_u \cdot T}\right) \left(P_{H_2O,\text{torr}}\right)$</td>
<td>* 1723 – 1973</td>
</tr>
<tr>
<td>(Greene and Finfrock 2001)</td>
<td>$1.89 \cdot \exp\left(-\frac{47.2 \text{ kcal mol}^{-1}}{R_u \cdot T}\right) \left(P_{H_2O,\text{torr}}\right)$</td>
<td>1073 – 1623</td>
</tr>
<tr>
<td>(Unal et al. 2000)</td>
<td>$7.60 \cdot \exp\left(-\frac{48.1 \text{ kcal mol}^{-1}}{R_u \cdot T}\right) \left(P_{H_2O,\text{torr}}\right)$</td>
<td>1073 – 1973</td>
</tr>
</tbody>
</table>

*Assumed to be derived from diffusion limited reaction rate data.
5.1.3.2 Effect of Molecular Nitrogen Addition

Given that $H_2$ inhibits the tungsten and water reaction, and dissociatively adsorbs into relatively strongly bound states at the surface (Chen et al. 2007b), it was hypothesized that $N_2$ may also affect oxidation rates since it has been theoretically shown that $WN(s)$ is a strongly bound state of nitrogen (Chen et al. 2009). This was tested experimentally in the TG flow reactor, results of which are shown in Fig. 5-20. The results clearly show there is no appreciable effect up to a $N_2$ to $H_2O$ ratio of 2.5, implying that transition energy barrier to break the $N≡N$ bond is too great for significant amounts of $WN(s)$ to be formed at the surface and inhibit oxidation rates. Previous adsorption studies also indicate that sticking probabilities − probability of a molecule chemisorbing onto a surface during a collision − of $N_2$ on a tungsten surface are reduced with increasing temperatures (Hayward et al. 1967; King and Wells 1974). This information also indicates that from the mechanisms presented Fig. 5-11 and Fig. 5-17, the reduction of surface oxides are more important than surface site blocking in oxidation rate reduction.

Figure 5-20: Effect of $N_2$ on the tungsten and $H_2O$ oxidation reaction.
5.1.3.3 Effect of Carbon Dioxide Addition

In many situations, tungsten may be oxidized by multiple species concurrently. This is particularly true in rocket nozzle erosion. It is not always clear how gas mixtures may affect chemical processes. In some cases, as shown previously, mixtures of various gases may lead to reduced oxidation rates, in others, such as mixtures of chlorine (Cl₂) and O₂, a synergistic effect may be taking place, leading to enhanced oxidation rates (Gordon and Brown 1962; Rosner and Allendorf 1967a). Experiments were conducted using the flow reactor to explore mixtures of CO₂ and H₂O to determine if any synergistic or inhibitive affects occur. At a constant H₂O partial pressure of 15.2 torr, CO₂ to H₂O ratios were varied between 0.25 and 4 (Fig. 5-21). The results indicate that there was very little effect of the additional CO₂; there is no indication of a inhibiting or strong coupling effect. Oxidation rates appear to increase slightly with increasing CO₂ partial pressures. Using Eq. 5-2 and Eq. 5-6, the oxidation rates are predicted by adding the associated rates for CO₂ and H₂O together. Given the experimental temperatures considered, the tungsten oxidation rate due to CO₂ is expected to be minimal to non-existent; therefore, if there is a synergistic effect between CO₂ and H₂O it would lead to a slight enhancement, however, the changes in rates are within experimental uncertainties of each other. It is clear from the results that there is no inhibiting effect of the CO₂ on the W and H₂O reaction at the temperatures and pressures considered.
5.2 Application to Rocket Nozzle Erosion

The implications of these results on rocket nozzle erosion were explored by considering a non-aluminized propellant, operating at potential motor conditions. Considering a simplified version of a common solid rocket propellant – 86.5 wt% ammonium perchlorate (AP) and 13.5 wt% hydroxyl-terminated polybutadiene (HTPB) – equilibrium calculations were performed using NASA’s CEA program to predict the concentrations of the product gases formed (Table 5-2). Using these conditions, Eq. 5-1, Eq. 5-3, and Eq. 5-6, the kinetically limited nozzle recession rates due to each oxidizer are predicted for the concentrations and temperatures found using CEA, assuming the tungsten density to be 19.25 grams per cm³ (Fig. 5-22). Since it was not known how \( H_2 \) affects \( CO_2 \) reactions, how \( CO \) affects \( H_2O \) reactions, or how both non-oxidizing species affect \( O_2 \) rates, it was assumed that...
there were no coupling effects between these sets of species for this analysis. Two nozzle surface temperatures are considered, estimated as being 400 and 600 K less than the equilibrium flame temperature, which was assumed to be the chamber temperature. Based on numerical modeling work from several researchers, both nozzle temperatures are believed to be reasonable approximations (Acharya and Kuo 2007a; Acharya and Kuo 2007b; Thakre and Yang 2009a).

The results clearly indicate $\text{H}_2\text{O}$ to be the dominant oxidizer under these motor conditions. Also illustrated are the acute effects $\text{H}_2$ have on inhibiting the tungsten and water reaction. At a $\text{H}_2$ to $\text{H}_2\text{O}$ ratio of approximately 0.2, the recession rate associated with $\text{H}_2\text{O}$ is reduced by 33 – 35% when considering the inhibiting effects of $\text{H}_2$, with a slightly greater influence at higher surface temperatures. Contrastingly, a $\text{CO}$ to $\text{CO}_2$ ratio of 1.5 caused the associated $\text{CO}_2$ recession rate to decrease by approximately 20 – 28%. When comparing the recession rates associated with $\text{H}_2\text{O}$ and $\text{CO}_2$ with that of $\text{O}_2$, it appears that under these conditions reactions involving $\text{O}_2$ may not be neglected without inducing appreciable errors or uncertainties, and at low pressures and surface temperatures $\text{O}_2$ may actually be more important than $\text{CO}_2$. However, any inhibiting effects of the $\text{O}_2$ and tungsten reaction are not included. Also illustrated in Fig. 5-22 is the keen temperature dependence of the corrosion rates, even in cases where the inhibiting effects of $\text{CO}$ and $\text{H}_2$ are included.

### Table 5-2: Equilibrium combustion temperatures and product species for AP / HTPB propellants.

<table>
<thead>
<tr>
<th>Motor Pressure [psi (MPa)]</th>
<th>Temp. [K]</th>
<th>$\text{H}_2\text{O}$</th>
<th>$\text{CO}_2$</th>
<th>$\text{O}_2$</th>
<th>$\text{OH}$</th>
<th>$\text{H}_2$</th>
<th>$\text{N}_2$</th>
<th>$\text{CO}$</th>
<th>$\text{HCl}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 (3.45)$^\dagger$</td>
<td>2881</td>
<td>0.382</td>
<td>0.0982</td>
<td>5.6E-04</td>
<td>0.008</td>
<td>0.0808</td>
<td>0.092</td>
<td>0.1484</td>
<td>0.176</td>
</tr>
<tr>
<td>1000 (6.89)$^\star$</td>
<td>2909</td>
<td>0.385</td>
<td>0.0991</td>
<td>3.6E-04</td>
<td>0.007</td>
<td>0.0799</td>
<td>0.092</td>
<td>0.1482</td>
<td>0.178</td>
</tr>
<tr>
<td>1500 (10.3)$^\ddagger$</td>
<td>2924</td>
<td>0.386</td>
<td>0.0995</td>
<td>2.7E-04</td>
<td>0.006</td>
<td>0.0794</td>
<td>0.092</td>
<td>0.1481</td>
<td>0.179</td>
</tr>
<tr>
<td>2000 (13.8)$^\star$</td>
<td>2933</td>
<td>0.387</td>
<td>0.0998</td>
<td>2.2E-04</td>
<td>0.005</td>
<td>0.0791</td>
<td>0.092</td>
<td>0.1480</td>
<td>0.180</td>
</tr>
<tr>
<td>1015 (7.0)$^\ddagger$</td>
<td>2812</td>
<td>0.379</td>
<td>0.097</td>
<td>-</td>
<td>0.001</td>
<td>0.097</td>
<td>0.092</td>
<td>0.157</td>
<td>0.170</td>
</tr>
</tbody>
</table>

$^\dagger$Values derived via NASA’s CEA software using an 87wt% AP – 13wt% HTPB propellant.

$^\star$Values derived by Haugen using an 83.5wt% AP – 14.4wt% HTPB – 2.1wt% unspecified additive propellant (Haugen 1998).

$^\ddagger$Values derived via NASA’s CEA software using an 87wt% AP – 13wt% HTPB propellant.
There is a limited amount of experimental data in the open literature describing the nozzle erosion rates of tungsten, however, measured erosion rates have been reported in the range of 0 to 0.14 mm/s, depending on motor conditions and preparation of the tungsten nozzle (Johnston et al. 1966; Haugen 1998). The highest erosion rate was found using a 65% dense tungsten nozzle. For near fully dense tungsten, erosion rates are reported to be 0 – 0.03 mm/s. The work from Haugen looked at erosion rates using a non-metalized AP/HTPB propellant, similar to the propellant formulation we have considered here (Haugen 1998). The work from Johnston et al. considered three propellants, two aluminized propellants and one AP-polyvinyl chloride propellant (Johnston et al. 1966). When using aluminized propellants with a fully dense tungsten nozzle no erosion of the tungsten nozzles were found over the entire test durations.

Recession rates were also predicted using the data provided by Haugen, who used an 83.5wt% AP and HTPB propellant (see bottom of Table 5-2) (Haugen 1998). As expected, the rates found using Haugen’s data corresponded well with the results using an 86.5wt% AP propellant; however, these rates do not match Haugen’s experimentally derived tungsten nozzle recession rates. Our predicted rates are more than double that found in the rocket
motor tests at the lower surface temperature considered, and an order of magnitude greater at the high surface temperature. Given these differences, it is implied that the oxidation reactions involved in nozzle erosion processes are either diffusion limited, kinetically limited due to lack of active sites (i.e., surface area) to oxidize, or an additional unknown inhibiting effect has not been considered. Oxidation rates may become less dependent or independent of the oxidizer concentration at high pressures as available surface sites become saturated, and sticking probabilities of oxidizing species are reduced considerably. As pressures increase within the rocket motor the partial pressure of oxidizing species increase, while the concentration of tungsten nozzle surface sites remain unchanged. Adsorption of oxidizing species onto a clean tungsten surface is known to be an exothermic, efficient and fast process, at higher surface coverage this process is less efficient. Desorption processes are generally endothermic and slower. Desorption of surface species or formations of higher surface oxides are therefore anticipated to be the kinetically limiting process in tungsten nozzle erosion. For this reason, high pressure oxidation processes such as those found in rocket motor erosion may not be accurately modeled using the simplified kinetic correlations developed thus far. A more detailed model and mechanism is required, or experimental rate data must be derived using much higher pressure conditions. The high temperatures and fast rates involved make the former solution a much more manageable and economic proposition for understanding the tungsten nozzle erosion problem.

Also considered was a hypothetical aluminized-AP and HTPB propellant. Details of this propellant’s equilibrium flame temperatures and product mole fractions are shown in Table 5-3. Using the same approach as above, throat recession rates were estimated and presented in Fig. 5-23. Some interesting effects of the aluminized propellant are realized due to the high flame temperatures, and large concentrations of CO and H₂. When the recession rates associated with H₂O were predicted without accounting for the inhibiting effects of H₂ extremely high recession rates were found, which were unrealistic given that little to no erosion was found with aluminized propellants and tungsten nozzles (Johnston et al. 1966; Opeka 2004). With the effects of H₂ considered, the rates of oxidation associated with H₂O were predicted to be much lower (<0.013 mm/s), due to the large H₂ to H₂O ratios (~2.4). In both plots, Fig. 5-23 indicates that CO₂ is as important as or more important of an oxidizer
than $H_2O$. This is because the $CO_2$ and tungsten reaction has a high activation energy, causing it to be quantitatively as important as the lower activation $H_2O$ reaction at high temperatures. Recession rates associated with $O_2$ appear to be an appreciable percentage of those of $CO_2$ and $H_2O$ when the inhibiting effects of $CO$ and $H_2$ are included, indicating that $O_2$ oxidation should not necessarily be neglected in the aluminized propellant case. However, as stated previously, any inhibiting effects $CO$ or $H_2$ may have on $O_2$ and tungsten reaction rates are not known at this time.

Table 5-3: Equilibrium combustion temperatures and product species for an aluminized AP / HTPB propellant.

<table>
<thead>
<tr>
<th>Motor Pressure [psi (MPa)]</th>
<th>Temp. [K]</th>
<th>$H_2O$</th>
<th>$CO_2$</th>
<th>$O_2$</th>
<th>$OH$</th>
<th>$H_2$</th>
<th>$N_2$</th>
<th>$CO$</th>
<th>$HCl$</th>
<th>$Al_2O_3$ (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 (3.45)*</td>
<td>3488</td>
<td>0.114</td>
<td>0.011</td>
<td>1.5E-04</td>
<td>0.010</td>
<td>0.276</td>
<td>0.078</td>
<td>0.212</td>
<td>0.127</td>
<td>0.085</td>
</tr>
<tr>
<td>1000 (6.89)*</td>
<td>3559</td>
<td>0.115</td>
<td>0.011</td>
<td>1.1E-04</td>
<td>0.009</td>
<td>0.281</td>
<td>0.078</td>
<td>0.214</td>
<td>0.129</td>
<td>0.086</td>
</tr>
<tr>
<td>1500 (10.3)*</td>
<td>3599</td>
<td>0.116</td>
<td>0.011</td>
<td>8.6E-05</td>
<td>0.008</td>
<td>0.284</td>
<td>0.079</td>
<td>0.215</td>
<td>0.131</td>
<td>0.086</td>
</tr>
<tr>
<td>2000 (13.8)*</td>
<td>3626</td>
<td>0.117</td>
<td>0.010</td>
<td>7.3E-05</td>
<td>0.007</td>
<td>0.286</td>
<td>0.079</td>
<td>0.216</td>
<td>0.131</td>
<td>0.087</td>
</tr>
</tbody>
</table>

* Values derived via NASA’s CEA software using a 69wt% AP – 19.5wt% Al – 11.5wt% HTPB propellant.

As with the cases presented in Fig. 5-22, predicted rates are much higher than what was found in real motors systems. This discrepancy could be due to phenomena that were not considered in the calculations. It is known with aluminized propellants, the liquid alumina ($Al_2O_3$) combustion products coat the nozzle surface, possibly serving as protective barrier against chemical attack. The second explanation was presented previously: oxidation rates at high pressures are diffusion or active surface site limited. Regardless of the mechanism that causes aluminized propellants to exhibit low or no erosion, Fig. 5-22 and Fig. 5-23 have provided a new perspective for rationalizing the method by which aluminized propellants reduce erosion rates. Generally it is considered that the primary reason for decreased erosion rates are reduced oxidizer concentrations, and other non-oxidizing species are not taken into account. However, if erosion rates have small oxidizer pressure dependence, the more important parameters are surface temperatures and ratios of $H_2$ to $H_2O$ and $CO$ to $CO_2$. Therefore, the primary importance of the aluminum is the production of $H_2$.
and CO, which are inhibitors of tungsten oxidation. Given the examples in Table 5-2 and Table 5-3, it is extremely difficult to reduce oxidizer concentrations by an order of magnitude; on the other hand, it was fairly easy to change the important species ratios by that much.

Figure 5-23: Estimated tungsten surface recession rates under rocket motor conditions using an aluminized-AP / HTPB propellant, assuming a surface temperature of: (a) $T_{\text{flame}} - 400$ K and (b) $T_{\text{flame}} - 600$ K.
Chapter 6
THEORETICAL MODELING AND MECHANISM DEVELOPMENT

Using the approach outlined in Fig. 2-6, several theoretical techniques have been utilized to decipher mechanisms involved in high temperature tungsten oxidation. Starting with thermodynamic calculations of equilibrium speciation, important reactants and product species were established, and intermediate surface species inferred. Along with well known gas- and bulk-phase species thermodynamics, density functional theory (DFT) calculations of adsorption and desorption from several sources have been used to estimate surface-species enthalpies, as well as the energetics of heterogeneous reactions. This chapter concludes with the presentation of a detailed kinetic reaction mechanism for the tungsten and oxygen reaction, which will become the foundation for future reaction mechanisms involving more complex oxidizing systems.

6.1 Thermodynamic Equilibrium Calculations

The use of thermodynamic calculations, as presented in Chapter 4, may be helpful when predicting important reaction products and intermediate species. Using NASA’s computer program, CEA (McBride and Gordon 1996), and the expanded thermodynamic database presented in Table 4-1, chemical equilibrium calculations were performed considering tungsten and single species oxidizers. Constant pressure equilibrium mole fractions of tungsten containing species as a function of temperature, using four different oxidizers – oxygen \((O_2)\), carbon dioxide \((CO_2)\), water \((H_2O)\), and nitrous oxide \((N_2O)\) – are illustrated in Fig. 6-1. Stoichiometries for these calculations were determined by assuming tungsten oxide formation of \(WO_3\) with excess oxygen (Eq. 6-1).

\[
W + Oxidizer \rightarrow WO_3 + \frac{3}{2}O_2 + X \quad (6-1)
\]
The results show a common theme amongst all systems, with solid, liquid, or gas-phase $WO_2$ and $WO_3$ (and its polymers) being the primary equilibrium species, the latter being the more dominant species under nearly all conditions considered in the above figure. However, in the tungsten-$H_2O$ system the presence of hydrogen creates a large amount of tungstic acid [$WO_2(OH)_2$], except at the lowest temperatures. Review of previous literature identified this as an important species during the corrosion of tungsten in the presence of $H_2O$ since the hydrated species formation increases volatility of tungsten oxides at lower temperatures (Promisel 1964; Greene and Finfrock 2001). Another interesting aspect of this

Figure 6-1: Equilibrium species for tungsten reactions involving simple oxidizers ($O_2$, $CO_2$, $H_2O$, and $N_2O$).
species is that its presence removes the appearance of liquid $WO_3$ from the equilibrium mixture. However, under higher pressure conditions, species such as $WO_{2(gr)}$ and $WO_{3(l)}$ are much more likely to be produced in appreciable amounts. The equilibrium calculations also show the formation of significant amounts of volatile oxides at approximately the same temperatures where continuous mass losses of tungsten were found in previous oxidation studies (~1600 K), as well as in this study. This was a good indication that equilibrium calculations are a valuable tool for predicting reaction behavior at high temperatures.

Equilibrium calculations were completed using the hydroxyl radical ($OH$) as well. Results yielded similar tungsten species formation as shown in the $W-H_2O$ system, indicating that tungstic acid is an important species in any high temperature oxidizing system containing hydrogen and oxygen. Although the $OH$ radical does not form in large amounts under most conditions, $OH$ may form noticeable concentrations in combustion product mixtures (see Table 5-3). An array of high temperature and pressure conditions found in rocket motors were studied using four propellant formulations, both metallized (aluminized) and non-metallized ammonium perchlorate (AP) and ammonium dinitramide (ADN) propellants with hydroxyl-terminated polybutadiene (HTPB) – a propellant fuel and binder material. Although these are common solid propellant materials, the formulations are not exactly as used in practice, mainly since propellant grains use other additives, and also because the exact chemical mixtures may change from batch to batch (particularly that of HTPB). The purpose of this study, which is presented and described in detail within Appendix B, is to determine the oxidation species of primary importance at a tungsten rocket nozzle surface. Results again indicated that $WO_2(OH)_2$, $(WO_3)_x = 1-3$, and $WO_2$ are primary tungsten oxidation products. However, AP propellants, which contain a large amount of chlorine, produced another primary oxidation species, tungsten oxychloride ($WO_2Cl_2$), which has been identified as an important oxidation species in $W-Cl-O$ mixtures in the past (Rosner and Allendorf 1967a). This oxychloride species presented itself in similar quantities, and illustrated similar temperature and pressure effects as the tungstic acid. Under most conditions, $WO_2Cl_2$ and $WO_2(OH)_2$ were by far the primary species. The formation of these two species during high temperature oxidation has not been studied thoroughly in the past, and therefore little is known regarding reaction mechanisms. Since previous studies have determined that $WO_2(OH)_2$ may decrease vaporization temperatures of tungsten oxides, it is
clear that $WO_2(OH)_2$ may form at solid surfaces. However, it is unclear if tungsten oxides of $WO_3$ or $WO_2$ will react homogeneously or heterogeneously (or in combination) to form the oxychloride and/or acid species under the high temperatures present in rocket motors. Resolution and clarity of this issue would provide a great benefit to this study. The results of the study presented in Appendix B also indicated that the kinetics of interest involving high pressure and temperature rockets could be found at lower pressures and temperatures since the types of species formation do not vary significantly. This provides some validity to extrapolating the results of this study to high temperatures and pressures, as was done in Chapter 5.

6.2 Surface-species Thermodynamics and Heterogeneous Reaction Energetics

Knowledge of species energetics (i.e., enthalpies of formation) provides an important baseline for theorizing chemical reaction mechanisms. Using individual species enthalpies, heat release and consumption quantities may be determined. With endothermic reactions, activation energies are at a minimum the heat consumed during a reaction (see Fig. 4-10). Unfortunately surface species energetics are not well understood, and not easily quantified because they may vary significantly depending on the substrate morphology. Using the theories described in 4.2.4 in conjunction with the gas-phase species enthalpies presented in Table 6-1, surface species enthalpies were estimated. Table 6-2 displays calculated enthalpies of relevant surface species that have been estimated using DFT simulations of adsorption on clean and pristine tungsten surfaces. All estimations were completed by assuming that the tungsten surface energetics are slightly less stable than bulk tungsten (i.e., $\Delta H_f, W(s) = 5$ kcal/mol). In several of the DFT studies, binding energy was defined at varying surface coverage and bonding locations, which may alter energetics considerably. In one such study the binding energy varied by more than 35 kcal/mol due to these modifications (Chen et al. 2007b). The highest surface coverage data were used for calculation of the values in Table 6-2, which more closely resemble higher pressure systems such as rocket motors. In nearly all cases there was good agreement between the different studies even though different crystallographic faces were considered in each one. It is worth noting that
$WC_{(s)}$ is greatly affected by surface bonding location in both studies which explored carbon containing reactions.

Table 6-1: Enthalpies of formation of gas-phase species relevant to surface-species enthalpy calculations.

<table>
<thead>
<tr>
<th>Gas-phase Species</th>
<th>$\Delta H_{\text{formation}}$ [kcal/mol (kJ/mol)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W$</td>
<td>203 (850)</td>
</tr>
<tr>
<td>$O$</td>
<td>59.5 (249)</td>
</tr>
<tr>
<td>$H$</td>
<td>52.1 (218)</td>
</tr>
<tr>
<td>$C$</td>
<td>171 (716)</td>
</tr>
<tr>
<td>$OH$</td>
<td>9.3 (39)</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>-57.8 (242)</td>
</tr>
<tr>
<td>$CO$</td>
<td>-26.4 (-111)</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>-94 (-394)</td>
</tr>
<tr>
<td>$WO$</td>
<td>101.5 (425)</td>
</tr>
<tr>
<td>$WO_2$</td>
<td>18.3 (76.6)</td>
</tr>
<tr>
<td>$WO_3$</td>
<td>-70 (-293)</td>
</tr>
<tr>
<td>$WO_2(OH)_2$</td>
<td>-216 (-904)</td>
</tr>
<tr>
<td>$WO_2Cl_2$</td>
<td>-160 (-670)</td>
</tr>
</tbody>
</table>

Source: (Chase 1998)

In the final two rows of the above Table 6-2, enthalpies of higher tungsten oxides were estimated. These results are derived from recent DFT calculations from Lin et al., whom collaborated in this research effort to learn the details of the high temperature oxidation process. A large degree of uncertainty is linked to these higher oxide values due to the difficulty in using molecular scale reaction energetics and applying them to a large scale physical parameter. A goal of chemical kinetics is to describe a molecular process in a simple manner that will predict large scale effects. Therefore, species may be described as $WO_{2(s)}$ and $WO_{3(s)}$, yet there is no definitive definition for the chemical structures of those species since electrons are shared between the oxygen and multiple tungsten atoms at the surface. For this reason, there is significant scatter in the calculated enthalpies shown in the following tables.
Table 6-2: Tungsten surface-species energetics derived from DFT adsorption modeling.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H_{\text{formation}}$ [kcal/mol]</th>
<th>Surface</th>
<th>Comments / Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$WO_{(s)}$</td>
<td>-94</td>
<td>$W(210)$</td>
<td>Calculated from dissociative $O_2$ adsorption; 1/6 ML surface coverage (Bligaard et al. 2004)</td>
</tr>
<tr>
<td></td>
<td>-98 (-94 a)</td>
<td>$W(100)$</td>
<td>Calculated from $O$ adsorption; 1/2 ML surface coverage (Scheijen et al. 2008)</td>
</tr>
<tr>
<td></td>
<td>-89</td>
<td>$W(111)$</td>
<td>Calculated from $O$ adsorption; 1 ML surface coverage; $\Delta H$ increases w/ surface coverage (Chen et al. 2007b; Chen et al. 2009)</td>
</tr>
<tr>
<td>$WH_{(s)}$</td>
<td>-10</td>
<td>$W(210)$</td>
<td>Calculated from dissociative $H_2$ adsorption; 1/6 ML surface coverage (Bligaard et al. 2004)</td>
</tr>
<tr>
<td></td>
<td>-28 (-12 b)</td>
<td>$W(111)$</td>
<td>Calculated from $H$ adsorption; 1 ML surface coverage (Chen et al. 2007b)</td>
</tr>
<tr>
<td>$WOH_{(s)}$</td>
<td>-82</td>
<td>$W(210)$</td>
<td>Calculated from $OH$ adsorption; 1/6 ML surface coverage (Bligaard et al. 2004)</td>
</tr>
<tr>
<td></td>
<td>-90</td>
<td>$W(111)$</td>
<td>Calculated from $OH$ adsorption; 1 ML surface coverage (Chen et al. 2007b)</td>
</tr>
<tr>
<td>$WCO_{(s)}$</td>
<td>-68</td>
<td>$W(210)$</td>
<td>Calculated from $CO$ adsorption; 1/6 ML surface coverage (Bligaard et al. 2004)</td>
</tr>
<tr>
<td></td>
<td>-59 (-51 a)</td>
<td>$W(111)$</td>
<td>Calculated from $CO$ adsorption; unspecified coverage (Chen et al. 2008b)</td>
</tr>
<tr>
<td></td>
<td>-59 (-91 c, -62 c,a)</td>
<td>$W(100)$</td>
<td>Calculated from $CO$ adsorption; 1 ML surface coverage (Scheijen et al. 2008)</td>
</tr>
<tr>
<td>$WH_2O_{(s)}$</td>
<td>-61 (-65 b)</td>
<td>$W(111)$</td>
<td>Calculated from $H_2O$ adsorption ($O$ bonds down); 1 ML surface coverage (Chen et al. 2007b)</td>
</tr>
<tr>
<td>$WCO_{2(s)}$</td>
<td>-127</td>
<td>$W(111)$</td>
<td>Calculated from $CO_2$ adsorption ($C$ and $O$ bond down); independent of surface coverage (Chen et al. 2008b)</td>
</tr>
<tr>
<td>$WC_{(s)}$</td>
<td>-36 (31 b)</td>
<td>$W(100)$</td>
<td>Calculated from $C$ adsorption; 1/2 ML surface coverage (Scheijen et al. 2008)</td>
</tr>
<tr>
<td></td>
<td>-12 (8 b)</td>
<td>$W(111)$</td>
<td>Calculated from $C$ adsorption; unspecified coverage (Chen et al. 2008b)</td>
</tr>
<tr>
<td>$WO_{2(s)}$</td>
<td>-154</td>
<td>$W(111)$</td>
<td>Calculated from dissociative $O_2$ adsorption, unspecified coverage (Lin et al. 2010)</td>
</tr>
<tr>
<td>$WO_{3(s)}$</td>
<td>-222</td>
<td>$W(111)$</td>
<td>Calculated from dissociative $O_2$ adsorption, unspecified coverage (Lin et al. 2010)</td>
</tr>
</tbody>
</table>

*Second most stable adsorption configuration.  b ¼ ML coverage.  c½ ML coverage.
As part of the same collaboration, Lin et al. also looked at desorption energetics of $WO_x = 1-3$, as well as adsorption and desorption of oxygen and water on an oxygen covered surface [$W(111)$]. Modeling results for desorption from clean and oxygen covered surfaces are summarized in Table 6-3. Again, as a caveat, the reactions in Table 6-3 are simplified to reflect large-scale processes. In all these DFT calculations, the adsorption process was exothermic followed by a highly endothermic desorption process of removing a tungsten atom from the surface. In cases of solely oxygen based species, adsorption was always highly exothermic (greater than 150 kcal/mol) – on both clean and oxygen covered surfaces – creating an overall exothermic reaction when $WO_2$ or $WO_3$ was the final product species, with $WO_3$ much more energetically favored. In the case that the surface was covered with oxygen, an activated adsorption process was found, with barriers as large as 20.4 kcal/mol. In all cases involving oxygen, desorption energies were greater than 120 kcal/mol. These results combined the experimentally derived global $E_a$ of 23.5 kilocalories suggests that if a single limiting reaction exists in tungsten oxidation by $O_2$, then the activated adsorption to form higher oxides is the limiting process.

### Table 6-3: DFT desorption energetics of $W$ and $O$ reactions from (Lin et al. 2010).

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction*</th>
<th>$\Delta H_{reaction}$ [kcal/mol]</th>
<th>Species</th>
<th>Calculated $\Delta H_{formation}$ [kcal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$W_{(b)} + WO_{(s)} \rightarrow W_{(s)} + WO$</td>
<td>172</td>
<td>$WO_{(s)}$</td>
<td>-65</td>
</tr>
<tr>
<td>2</td>
<td>$W_{(b)} + WO_{2(s)} \rightarrow W_{(s)} + WO_2$</td>
<td>154</td>
<td>$WO_{2(s)}$</td>
<td>-131</td>
</tr>
<tr>
<td>3</td>
<td>$W_{(b)} + WO_{3(s)} \rightarrow W_{(s)} + WO_3$</td>
<td>142</td>
<td>$WO_{3(s)}$</td>
<td>-207</td>
</tr>
<tr>
<td>4</td>
<td>$W_{(b)} + 3WO_{3(s)} \rightarrow 3WO_{2(s)} + WO_3$</td>
<td>67.1</td>
<td>$WO_{3(s)}$</td>
<td>-177 $^b$ (-200 $^c$)</td>
</tr>
<tr>
<td>5</td>
<td>$W_{(b)} + 2WO_{3(s)} \rightarrow WO_{(s)} + WO_{2(s)} + WO_3$</td>
<td>123</td>
<td>$WO_{3(s)}$</td>
<td>-195 $^b$ (-220 $^c$)</td>
</tr>
</tbody>
</table>

* SURFACE CHEMKIN formalism. $^b$ Using species enthalpies calculated in reactions 1-2. $^c$ Using Table 6-2 values.

Calculations involving $H_2O$ indicate much lower heat releases upon adsorption (~30 kcal/mol), but they still involve highly endothermic desorption processes, yielding a combined endothermic reaction (see Fig. 6-2). Desorption of $WO_2(OH)$ was determined in the study from Lin et al. to be the most energetically favorable process involving a tungsten species – only 57.9 kcal/mol endothermic from a $O$ covered surface. It can be envisioned that this species may then react further to form tungstic acid. Since the energetics of this
The desorption process is close to the global $Ea$ found experimentally, this may imply that this desorption process is in the limiting oxidation step.

Calculations of individual species thermodynamics are taken a step further by estimating the energetics of reaction processes that have not been estimated using quantum chemical theories. Table 6-4 outlines several reaction processes that may be important in

![Figure 6-2: Potential energy surface of $H_2O$ adsorption and subsequent desorption on a partially (top) and fully covered (bottom) $W(111)$ surface, source: (Lin et al. 2010).](image-url)
global tungsten oxidation processes. Several reactions are postulated in Chapter 5 as oxidation inhibition reactions (5.1.2.1 and 5.1.3.1, reactions 1–8). These reaction energetics estimations support the suggested inhibition mechanism, as all are exothermic in the direction that would lead to corrosion inhibition – though activation barriers for these reactions are unknown. Others reactions shown are important adsorption and desorption processes, of which the desorption process is endothermic.

Table 6-4: Estimations of heterogeneous reaction energetics.

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>$\Delta H_{\text{reaction}}$ [kcal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$W(s) + CO \rightleftharpoons WCO(s)$</td>
<td>-43</td>
</tr>
<tr>
<td>2</td>
<td>$W(s) + WCO(s) \rightleftharpoons WO(s) + WC(s)$</td>
<td>-47</td>
</tr>
<tr>
<td>3</td>
<td>$WO_2(s) + CO \rightleftharpoons WO(s) + CO_2$</td>
<td>-7</td>
</tr>
<tr>
<td>4</td>
<td>$WO_3(s) + CO \rightleftharpoons WO_2(s) + CO_2$</td>
<td>-11</td>
</tr>
<tr>
<td>5</td>
<td>$2W(s) + H_2 \rightleftharpoons 2WH(s)$</td>
<td>-48</td>
</tr>
<tr>
<td>6</td>
<td>$2WO(s) + H_2 \rightleftharpoons 2WOH(s)$</td>
<td>-19</td>
</tr>
<tr>
<td>7</td>
<td>$WO_2(s) + H_2 \rightleftharpoons WO(s) + H_2O$</td>
<td>3</td>
</tr>
<tr>
<td>8</td>
<td>$WO_3(s) + H_2 \rightleftharpoons WO_2(s) + H_2O$</td>
<td>-1</td>
</tr>
<tr>
<td>9</td>
<td>$W(s) + OH \rightleftharpoons WOH(s)$</td>
<td>-100</td>
</tr>
<tr>
<td>10</td>
<td>$WO(s) + OH \rightleftharpoons WO_2(s) + H$</td>
<td>-18</td>
</tr>
<tr>
<td>11</td>
<td>$2W(s) + CO_2 \rightleftharpoons WO(s) + WCO(s)$</td>
<td>-61</td>
</tr>
<tr>
<td>12</td>
<td>$2W(s) + H_2O \rightleftharpoons WH(s) + WOH(s)$</td>
<td>-57</td>
</tr>
</tbody>
</table>

* Using forward reaction direction; mean value presented using range of numbers from Table 6-2 and Table 6-3.

6.3 Numerical Modeling of the Tungsten and Oxygen Reaction

Using the experimental results in Chapter 5, as well as the theoretical developments of the preceding two sections, the numerical flow reactor model (see 4.2) was used to derive an oxidation mechanism. The model, which was written using FORTRAN 77, is presented at length in Appendix D.

Before mechanisms could be postulated, an extremely important parameter of the model had to be determined, the surface site density ($\Gamma$). This parameter is directly related to
global reaction rates, and is often and incorrectly unprovided in literature that presents detailed heterogeneous kinetics. This parameter is particularly influential in high pressure systems, or systems limited by available reaction sites. Using a lattice parameter of 3.19 Å (Ross and Hume-Rothery 1963), the surface site (i.e., on-top atom) density of three surfaces were determined. Given that tungsten is a body-centered-cubic (BCC) metal, site densities of $9.43 \times 10^{-10}$, $2.31 \times 10^{-9}$, and $1.63 \times 10^{-10}$ were construed for $W(111)$, $W(110)$, and $W(100)$ surfaces, respectively. Although many of the estimated thermodynamics have been estimated from $W(111)$ surfaces, $W(110)$ is the most energetically favorable due its high coordination, and should be present in the highest concentrations of a bulk polycrystalline tungsten material. For this reason, the $\Gamma$ of the $W(110)$ surface was used in all subsequent calculations.

Using the information garnered from chemical equilibrium, DFT, and the experimental results of this study and others, a chemical mechanism of tungsten oxidation by $O_2$ was conceived. Given spectroscopic studies, under the conditions of this investigation, $WO_2$ and $WO_3$ were expected to be the primary desorption species, with greater amounts of $WO_2$ at higher temperatures (> 2000 K). Afforded the quantum mechanics studies presented above, it is well accepted that adsorption processes are highly exothermic; however, these processes may require significant energy to surpass an activation barrier. In all tungsten species desorption processes (corrosion), highly endothermic reactions were found. When brought together, the current knowledge of the oxidation process provides two interpretations of the oxidation process.

In the first interpretation, the formation of higher surface oxides due to an activated adsorption is the limiting tungsten oxidation reaction under the conditions considered in this work. As such, this limiting chemical route should exhibit an activation energy close to that of the global process. While the second interpretation is that the tungsten oxidation process is limited by several high activation energy desorption reactions, including corroding ($WO$, $WO_2$, $WO_3$) and non-corroding processes ($O$, $O_2$). The sum of these chemical progressions yield an apparent activation energy for the global corrosion reaction equal to that found in this study (23.5 kcal/mol).
In this dissertation, the first interpretation was used due to the supporting DFT information. Given the overall lack of detailed understanding of the chemical processes, the initially proposed model was simplified to include only \( WO_3 \) as a desorbing species (Table 6-5). This was justified by the equilibrium calculations. When no hydrogen or chlorine is present, \( WO_3 \) and its polymers are the primary product species; at the high temperatures considered, if \( WO_2 \) was desorbing from the surface in appreciable quantities, it should be rapidly oxidized to a higher oxide in the near surface region.

**Table 6-5: Simplified tungsten-\( O_2 \) high temperature oxidation kinetic mechanism.**

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>( A ) [mols, cm, sec]</th>
<th>( \beta )</th>
<th>( E ) [kcal/mol]</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( 2W(s) + O_2 \rightarrow 2WO_2(s) )</td>
<td>( 9.0 \times 10^{20} )</td>
<td>0.5</td>
<td>0.0</td>
<td>Estimated using Eq. 4-17</td>
</tr>
<tr>
<td>2</td>
<td>( 2WO_2(s) + O_2 \rightarrow 2WO_3(s) )</td>
<td>( 9.0 \times 10^{20} )</td>
<td>0.5</td>
<td>0.0</td>
<td>Estimated using Eq. 4-17</td>
</tr>
<tr>
<td>3</td>
<td>( WO(s) + O \rightarrow WO_2(s) )</td>
<td>( 2.9 \times 10^{12} )</td>
<td>0.5</td>
<td>0.0</td>
<td>Estimated using Eq. 4-17</td>
</tr>
<tr>
<td>4</td>
<td>( WO_2(s) + O \rightarrow WO_3(s) )</td>
<td>( 2.9 \times 10^{12} )</td>
<td>0.5</td>
<td>0.0</td>
<td>Estimated using Eq. 4-17</td>
</tr>
<tr>
<td>5</td>
<td>( 2WO_2(s) + O_2 \rightarrow 2WO_3(s) )</td>
<td>( 3.1 \times 10^{20} )</td>
<td>0.5</td>
<td>23.0</td>
<td>Empirically matched to experimental data</td>
</tr>
<tr>
<td>6</td>
<td>( WO_2(s) + W(s) \rightarrow 2WO(s) )</td>
<td>( 8.7 \times 10^{18} )</td>
<td>1.0</td>
<td>5.0</td>
<td>Estimated as ( \Gamma ) modified Eq. 4-18</td>
</tr>
<tr>
<td>7</td>
<td>( WO(s) + WO(s) \rightarrow 2WO_2(s) )</td>
<td>( 8.7 \times 10^{18} )</td>
<td>1.0</td>
<td>5.0</td>
<td>Estimated as ( \Gamma ) modified Eq. 4-18</td>
</tr>
<tr>
<td>8</td>
<td>( WO_2(s) \rightarrow WO(s) + O )</td>
<td>( 2.0 \times 10^{10} )</td>
<td>1.0</td>
<td>121.0</td>
<td>Estimated using Eq. 4-18 and mean energetics from tables above</td>
</tr>
<tr>
<td>9</td>
<td>( WO_3(s) \rightarrow WO_2(s) + O )</td>
<td>( 2.0 \times 10^{10} )</td>
<td>1.0</td>
<td>117.0</td>
<td>Estimated using Eq. 4-18 and mean energetics from tables above</td>
</tr>
<tr>
<td>10</td>
<td>( W_{(b)} + 3WO_3(s) \rightarrow 3WO_2(s) + WO_3 )</td>
<td>( 6.5 \times 10^{27} )</td>
<td>1.0</td>
<td>67.0</td>
<td>Empirically matched to experimental data, with ( E ) from Table 6-3</td>
</tr>
</tbody>
</table>

Using the mechanism above with the numerical model, predicted corrosion rates of tungsten are presented in Fig. 6-3, which matches the experimental data very well. Since gas-phase diffusion was not accounted for in the model, the diffusion limitations in the experimental data are not depicted in the model. Given the range of conditions considered, reactions involving \( O \) may be removed, providing an equally accurate model; however, these
reactions were deemed necessary if the model is to be used at the higher temperatures, such as present in rocket motors.

Further information was acquired from the model by exploring the transient response of the system as functions of temperature. The gas-phase mole fractions are presented in Fig. 6-4, while the surface site fractions are shown in Fig. 6-5. In both systems, steady-states were quickly reacted. In the gas-phase, there is a dip in the O\textsubscript{2} concentration as the surface, which was initially clean, was covered by multiple layers of oxygen. Since the system was limited by WO\textsubscript{3(s)} formation, after the tungsten surface became covered by WO\textsubscript{2(s)}, the O\textsubscript{2} concentration stabilizes. At the temperatures considered, concentrations of O were negligible. As would be anticipated, concentrations of WO\textsubscript{3} were greater at higher temperatures, whereas surface concentrations of WO\textsubscript{3(s)} were reduced.

Future studies will be required in order to build multiple desorption species into the model. Further, more detailed understanding of the W-O\textsubscript{2} system will allow the development of multiple oxidizer systems.
Figure 6-4: Numerical model predicted gas-phase mole fractions.

Figure 6-5: Numerical model predicted surface site fractions.
Chapter 7
SUMMARY AND CONCLUSIONS

The following chapter summarizes the important developments of this dissertation. Included is a categorization of the primary conclusions drawn from: chemical equilibrium studies of tungsten oxidation, global reaction kinetics found using the thermogravimetric (TG) flow reactor, and mechanisms derived using the numerical model of the flow reactor. Combined, these conclusions are used to pass judgment on the mechanisms of tungsten rocket nozzle erosion.

7.1 Thermodynamic Equilibrium

Analysis of the thermodynamic equilibrium conditions of tungsten oxidation indicated that $WO$, $WO_2$, and $\{(WO_3)_x = 1-3\}$, were the primary product species. As temperatures increased smaller oxide species were more likely to be dominant. This result was supported by experimental spectroscopic studies. When hydrogen or chlorine added to the oxidizing system, new product species were formed that were generally more important that other oxides, particularly at high temperatures. These species included tungsten oxychloride ($WO_2Cl_2$) and tungstic acid [$WO_2(OH)_2$]. Tungsten chlorides (e.g., $WCl_4$, $WCl_6$) were not found at high temperatures and pressures. Using these results, under most conditions purely vapor-phase tungsten oxides are expected to form at temperatures greater than 1500 K, unless oxidation occurs at high pressure (> 1 atm) or in an environment free of hydrogen, chlorine, or other species with high affinities for oxygen.

The pressure dependence of predicted equilibrium species indicated that many of the same species and relative concentrations occur at atmospheric conditions as they do at high pressures, such as those found in rocket motors. This conclusion suggests that many of the same chemical reaction mechanisms exist over a wide pressure range; therefore, justification exists for extrapolating lower pressure experimental results and theoretical modeling to high pressure conditions.
Relative oxidation of the tungsten may be reduced by adding species with a greater affinity for bonding to oxygen (e.g., aluminum). Inclusions of species that are highly favorable for redox reactions reduce the concentrations of oxidizing species, yielding non-reactive by-products that can have auspicious implications in applications where reduced levels of tungsten corrosion are desired, such as rocket nozzles.

7.2 Thermogravimetric Flow Reactor

Using a TG flow reactor, kinetically limited oxidation rates of tungsten have been investigated at temperatures as high as 1700°C. Several oxidizers were explored, including oxygen ($O_2$), carbon dioxide ($CO_2$), and water ($H_2O$). Several other species have been considered that did not oxidize tungsten or lead to corrosion, but did have significant consequences regarding oxidation kinetics. In the presence of $H_2$, $H_2O$ corrosion rates were dramatically reduced. A similar but lesser effect occurred when increasing concentrations of carbon monoxide ($CO$) were including with $CO_2$. Empirical correlations have been developed for all of these oxidation processes and are expressed in Eq. 7-1 ($O_2$, also Eq. 5-1), Eq. 7-2 ($H_2O$ and $H_2$, also Eq. 5-6), and Eq. 7-3 ($CO_2$ and $CO$, also Eq. 5-3). Each equation is given in order of increasing activation energy, and decreasing oxidizer pressure dependence. Correspondingly, $O_2$ produces the fastest reaction kinetics under most conditions, followed by $H_2O$ and then $CO_2$, assuming constant partial pressures. Mechanisms for the inhibiting processes of $CO$ and $H_2$ were postulated as surface oxide reduction, or surface site blocking, with the former being the more likely scenario.

\[
i_{W-O_2} \left[ \frac{\text{grams of W}}{\text{cm}^2 \text{sec}} \right] = 6.99 \times 10^{-2} \cdot \exp \left( \frac{-23.5 \text{ kcal/mol}}{R_u \cdot T} \right) \left( \frac{P_{O_2, \text{torr}}}{P_{H_2O, \text{torr}}} \right)^{0.89} \tag{7-1}\]

\[
i_{W-H_2O,H_2} \left[ \frac{\text{grams of W}}{\text{cm}^2 \text{sec}} \right] = 9.29 \cdot \exp \left( \frac{-50.9 \text{ kcal/mol}}{R_u \cdot T} \right) \left( \frac{P_{H_2O, \text{torr}}}{P_{H_2, \text{torr}}} \right)^{0.82} \times \exp \left[ (6.86 - 1.14 \cdot \ln T) \left( \frac{P_{H_2}}{P_{H_2O}} \right) \right] \tag{7-2}\]

\[
i_{W-CO_2,CO} \left[ \frac{\text{grams of W}}{\text{cm}^2 \text{sec}} \right] = 2.54 \cdot \exp \left( \frac{-64 \text{ kcal/mol}}{R_u \cdot T} \right) \left( \frac{P_{CO_2, \text{torr}}}{P_{CO_2}} \right)^{0.6} \times \exp \left[ -2.194 \times 10^{11} \cdot T^{-3.574} \left( \frac{P_{CO}}{P_{CO_2}} \right) \right] \tag{7-3}\]
Other flow reactor studies explored the influence of nitrogen on the $H_2O$ reaction, which was deemed negligible, and mixtures of $H_2O$ and $CO_2$. The former lends further credence to surface oxide reduction being the primary inhibiting mechanism involving $CO$ and $H_2$. The latter studied revealed that there was no synergism between the two oxidizers that would lead to substantially reduced or increased oxidation rates; indicating that an additive approach may be appropriate for describing high temperature corrosion in a mixture of the two oxidizers.

7.3 Rocket Nozzle Erosion Application

Given the outcome of the experimental results, correlations were extrapolated to the higher temperature and pressure conditions of rocket motors. The product of this analysis indicated that under the extremely high pressures of rocket motors, nozzle corrosion rates are likely to be limited by either mass transfer processes, or desorption processes. At high pressures, nozzle surfaces become saturated with oxides, reducing the pressure dependence of reactions from those indicated in the abovementioned kinetic correlations. These limiting processes are more likely to occur with non-aluminized solid rocket propellants, which produce large concentrations of oxidizing species (primarily $H_2O$ and to a lesser extent $CO_2$), and considerably smaller quantities of $H_2$ and $CO$. Aluminized propellants yield significantly higher temperatures, which can exponentially increase corrosion rates; however, the presence of the aluminum reduces oxidizing species concentrations, and more importantly, increases concentrations of non-oxidizing inhibiting species. The influence of the inhibiting species slow the kinetic rates considerably, possibly to the extent that kinetically limited reactions can occur. The consideration of non-oxidizing species as being as important as oxidizers is a new methodology for understanding these heterogeneous processes, which will lead to important advancements moving forward.
7.4 Theoretical Modeling and Mechanism Development

Using a numerical model of the flow reactor used in this study, as well as density functional theory (DFT) studies from other researchers, several results have been obtained. It is clear that the adsorption reactions involved in tungsten oxidation are very exothermic in nature, whereas desorption processes are highly endothermic. That said, DFT has indicated that adsorption can be an activated process when the tungsten surface is oxidized. Assuming formation of higher surface oxides to be the limiting reaction during oxidation by $O_2$, and $WO_3$ to be the only desorption species over the range of temperatures of consideration, experimental results were predicted with satisfactory levels of accuracy. When $CO_2$ and $H_2O$ are added to the oxidizing system, multiple limiting processes may exist. Additionally, the presence of $H_2$ and $CO$ may limit the process by several means, including: reduction of surface oxides and blocking of reaction sites, both of which have been verified to be energetically favorable reaction processes.
Chapter 8

RECOMMENDATIONS AND FUTURE WORK

Several potential experimental and theoretical topics to be considered in the future, which are related to this research study are listed in the following sections. These topics involve using the tools and expertise developed over the course of this work to explore new materials, as well as areas relating to chemical reactions of tungsten at high temperature. Although many questions have been answered with this work, many more should be answered to gain a thorough understanding of the chemical kinetics and reaction mechanisms, particularly those pertaining to multiple species systems. Many of the recommended avenues for future research will require multidisciplinary knowledge of thermodynamics, physical chemistry, fluid dynamics and heat transfer, as well as teams of experimentalists, modelers, and theoreticians. As primarily an experimental study, this and future work should be used by modelers as an initial roadmap for exploring details of tungsten oxidation and other high temperature heterogeneous processes.

8.1 Thermogravimetric Flow Reactor Modifications and Analysis

At the conclusion of this dissertation, procedures and precautions have been refined significantly from the initial construction of the large scale thermogravimetric (TG) flow reactor used in this research investigation. Future studies may benefit significantly from the availability of this reactor and the knowledge gained through this dissertation. Research projects that are recommended to be pursued with this system are:

1. Investigate new materials using nearly the identical procedure as used in this dissertation. Materials of interest that may be studied are: molybdenum, hafnium, tantalum, rhenium, or multiple element compounds such as carbides. Initial studies have begun with graphite, results of which are presented in Appendix A.

2. Expand the oxidizer concentration range to higher partial pressures.
3. Examine mixtures of oxidizing and non-oxidizing species that have not been considered to date (e.g., $O_2$, $HCl$, $CO_2$, $H_2O$).

4. Expand the temperature range and operating conditions at which the TG flow reactor may operate by incorporating a new heating device that uses an RF induction heater.
   a. Using the induction heater, which only heats electrically conductive materials, quantify the effects of $CO$ on the $H_2O$ and $O_2$ oxidation reactions, as well as the effect of $H_2$ on the $CO_2$ and $O_2$ reactions.
   b. Alumina flow reactor tubes soften at high temperatures, restricting their ability to withstand pressure differentials. Using a fused quartz reactor tube with the induction heater, investigate the effects of altering overall system pressures on the reaction kinetics.

8.2 Chemical Spectroscopy Investigations

Several questions remain at the conclusion of the dissertation due to the unidentified chemical makeup of species desorbing from the surface. A good consensus exists regarding the tungsten and $O_2$ reaction system (Berkowitz-Mattuck et al. 1963; Schissel and Trulson 1965; Azens et al. 1995); however, there are several unknowns when a third species or element is involved. The use of chemical spectroscopy to explore these reactions will enable newer, more accurate mechanisms to be developed, and will also provide experimental data for validation of computational predictions. The primary recommended topic for future research in this field is the utilization of mass-spectroscopy (MS) techniques under vacuum conditions with molecular beams of $CO_2$ and $OH$ to measure the desorbing species concentrations coming from a heated tungsten surface. The use of $CO_2$ will confirm or deny a previous study indicating very little $WO_3$ is formed (Aspinall 1965). Use of the hydroxyl radical will determine if tungstic acid $[WO_2(OH)_2]$ or a similar species is formed at the surface or homogeneously at high temperature. Mixtures of oxidizers and non-oxidizing inhibiting species may also be considered to shed light on the inhibition mechanisms.
8.3 Theoretical Modeling and Mechanism Development

Several areas are recommended for future exploration involving theoretical modeling approaches. These include further development of mechanisms and kinetics using the numerical flow reactor model created as part of this work, and also further quantum mechanic (QM) predictions using techniques such as density functional theory (DFT). In some instances QM modeling of high temperature processes is necessary to resolve questions regarding the chemical mechanisms.

1. Using a QM model, portray the following surface reaction (heterogeneous) processes:
   a. Desorption of oxidized tungsten surfaces – pristine and defective – in the presence of $H$ and $C$ species. Does tungstic acid desorb directly from the surface?
   b. Adsorption of $O_2$, $CO_2$, $OH$, and $H_2O$ on clean tungsten surfaces containing defects. Of particular interest are tungsten hydroxide formation routes.
   c. Adsorption of $O_2$, $CO_2$, $OH$, and $H_2O$ on an oxygen covered tungsten surfaces. Explore effects of varying concentrations of $H$ and $C$ as well.

2. Using a QM model, develop homogeneous reaction kinetics so that gas-phase tungsten species reactions may be included in future models:
   a. Model energetic and kinetic processes involving the reaction between tungsten oxides ($WO_x = 1-3$) and various hydrogen containing species ($H$, $OH$, $H_2$, $H_2O$). These reactions may be important as the formation of tungstic acid can reduce near-surface oxidizing species concentrations.
   b. Predict kinetics of tungsten oxide oxidation reactions that may be of interest in high temperature energy systems (e.g., $WO_x = 1,2 + CO_2 \leftrightarrow WO_x = 2,3 + CO$).

3. As new information becomes available, using the experimentally derived global reaction rates and the numerical TG flow reactor model, develop more advance chemical mechanisms and kinetics. Of particular interest would be the accurate description of $H_2O$, $H_2$, and bulk $W$ reactions.
8.4 Tungsten Rocket Nozzle Erosion Minimization Approach

Results from this research study have been very helpful in developing an understanding of the corrosion processes associated with tungsten rocket nozzles. Moving forward it is recommended that the empirical correlations developed be implemented into existing multidimensional numeric models. The use of the correlations derived here would be the first step taken with these types of models to account for the effects of CO and H$_2$ on the corrosion processes. The results of this study indicate that the formation of these inhibiting species may be a driving factor in the reduced erosion rates of aluminized propellants. Combined with numerical modeling approaches, a parametric experimental study using a rocket motor simulator – such as the one constructed in the High Pressure Combustion Laboratory (HPCL) at The Pennsylvania State University (Evans et al. 2006; Evans et al. 2007; Evans et al. 2009) – would provide a significant amount of knowledge regarding nozzle corrosion processes. The conclusions generated in the dissertation also indicate that the use of a material that produces large quantities of H$_2$ upon thermal decomposition in a nozzle boundary-layer control system (NBLCS) may provide an advantage. The current NBLCS design decomposes center-perforated grains of ablative materials (made of succinic acid and poly-vinyl acetate) to produce high concentrations of CO, and has performed well at the task of reducing graphite nozzle erosion. It is unknown if H$_2$ may perform more efficiently at this task, but evidence suggests it may. It is recommended that modeling and experiments explore the use of high hydrogen content grains in place of the existing ones for relative comparisons of performance.
BIBLIOGRAPHY


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Appendix A

HIGH TEMPERATURE REACTIONS OF SYNTHETIC GRAPHITE

Graphite, a common allotrope of carbon (C), occurs naturally but is ordinarily manufactured for industrial use. Its thermal and electrical conductivity, strength, low density, and good resistance to heat in the absence of oxidizing compounds make it an appealing material for a number of applications. Synthetic graphite is generally fabricated using coal tar pitch, petroleum coke, and other carbonaceous solid particles. These materials are heated to high temperature under pressure, graphitizing the materials together. Depending on the application, this process is often repeated several times to increase density and reduce porosity. Steps may also be taken to remove inorganic impurities from the graphite, which can enhance oxidation rates of the material (Breval et al. 2002).

Like tungsten (W), graphite is a material used for solid rocket nozzles. Due to its relatively lower cost, density, and ease of machining, graphite is more commonly used than W. However, graphite also is very susceptible to erosion due to high temperature oxidation, as well as ablation of the material itself. In these cases, nozzle throat recession rates may be extremely high, particularly due to its low density. When oxidized, gas-phase oxides are formed, most commonly carbon monoxide (CO) and carbon dioxide (CO₂). Generally, CO is the primary desorbing species, depending on the gas-phase atmosphere (Eq. A-1 and Eq. A-2). Another high temperature application in which graphite is commonly used is nuclear reactors, specifically for fuel sleeves and reflectors. Since graphite is a form of carbon, much of what is learned from its chemical reaction processes can also be applied to the combustion of coal and charcoal. In all applications, the principle oxidizing environments of interest are air (oxygen, O₂), CO₂, and steam (H₂O).

\[
C(s) + CO_2 \rightleftharpoons CO + CO \quad (A-1)
\]

\[
C(s) + H_2O \rightleftharpoons CO + H_2 \quad (A-2)
\]
In comparison to $W$, which can have a multitude of oxidation products, the graphite oxidation mechanism is much simpler. However, many facets of the high temperature reactions of graphite are still not understood. Several steps were taken during this dissertation to shed some light on these misunderstandings.

A.1 Overview of Graphite Rocket Nozzle Erosion

Since graphite is a commonly used nozzle material, several theoretical and experiment evaluations of the chemical erosion processes exist (Bartlett 1963; Heath and Thackray 1969; Jones et al. 1986; Kuo et al. 2005; Evans et al. 2006; Acharya and Kuo 2007b; Acharya and Kuo 2007a; Evans et al. 2007; Thakre and Yang 2008a; Bianchi et al. 2009; Evans et al. 2009; Thakre and Yang 2009b). Many of these studies were conducted recently due to a renewed emphasis on understanding and mitigating these processes so that motors can operate at higher temperatures and pressures. As with other systems, the majority of the published results and discoveries are related to theoretical models, as opposed to the experimental evaluations. This is due to the sensitive nature of propellant formulations and performance, as well as the added costs and complexities of actual rocket firings.

Much of the early work on graphite nozzle erosion was done at the Air Force Rocket Propulsion Laboratory at Edwards Air Force Base in California using BATES (Ballistic Test and Evaluation System) motors (Geisler 1981; Geisler and Beckman 1998). Thousands of tests were completed with these test motors starting in the early 1960’s, learning much about motor operation and nozzle material performance, particularly graphite and C-C composite materials. At the high temperatures and pressures of rocket motors it was determined that $H_2O$ and $OH$ are the most important oxidizing species in solid rocket motors; however, it was also determined that under most conditions diffusion limited corrosion processes occur. Although there is no doubt that $H_2O$ appears at highest concentrations of all oxidizing species in most solid rockets, several chemical kinetic measurements indicate that $CO_2$ is just as important in terms of its relative kinetics (Golovina 1980; Libby and Blake 1981; Culbertson and Brezinsky 2009). Typical nozzle throat erosion rates were determined to be on the order of 0.05 to 3.5 mm/s, depending on nozzle temperatures, combustor pressures, and propellant composition. It was also determined that aluminized propellants yield lower erosion rates,
even though temperatures were increased. This is often attributed to reduced concentrations of $H_2O$ in the exhaust stream. This dissertation has shown that the presence of aluminum can significantly increase concentrations of $H_2$ and $CO$, which can significantly reduce tungsten oxidation rates. An equivalent type of oxidation inhibition mechanism may occur with graphite (Jones et al. 1986).

A correlation was developed for the quick prediction of nozzle erosion rates (Eq. A-3); this correlation is strictly a function of the molar $H_2O$ concentration ($M_w$, %), and the chamber pressure ($P_c$). This correlation is contingent upon the surface temperature being above 2600 K; at this temperature surface recession rates were found to increase significantly due to increased graphite decomposition rates. At the time, it was determined that a new carbon allotrope called carbine was formed above this temperature, though this has never been proven.

$$R_c[\text{mils/s}] \approx 0.58 \cdot M_w \left( \frac{P_c}{1000} \right)^{0.8} \quad (A-3)$$

In a more recent series of tests, Evans et al. have used a high pressure solid rocket motor simulator, as well an end-burning solid rocket motor to measure motor and nozzle erosion performance (Evans et al. 2006; Evans et al. 2007; Evans et al. 2009). Using an X-ray translucent nozzle setup to measure simultaneous recession rates at average chamber pressures from 3 to 21 MPa (435 – 3045 psi), throat erosion rates have ranged from 0 to approximately 3.5 mm/s. Negligible erosion rates were found using a nozzle boundary layer control system (NBLCS), which used hot combustion gases to decompose succinic acid and polyvinyl acetate to produce a relatively cool gas stream of $CO$ rich gases in the nozzle’s boundary layer, cooling the nozzle surface and reducing oxidation rates.

The theoretical modeling completed in recent years has generated a significant amount of knowledge, but growth in this area has also been hindered by the relative lack of understanding and conflicting reports regarding high temperature reactions of graphite. Acharya and Kuo have conducted several studies of metallized and non-metallized AP (ammonium perchlorate) and HTPB (hydroxyl-terminated polybutadiene) propellants and their interactions with graphite nozzles at chamber pressures between 7 and 55 MPa (1000 – 8000 psia) (Acharya and Kuo 2007b; Acharya and Kuo 2007a). These studies predicted
nozzle erosion rates with varying degrees of accuracy, depending on the kinetic correlations used. Mechanical erosion effects were neglected since they were deemed secondary to chemical erosion in graphite nozzle systems, particularly when non-metallized propellants are used. Depending on the motor conditions, both kinetic and diffusion limited erosion rates were found. In general, diffusion limited conditions prevailed at higher pressures and temperatures. Metallized propellants produced diffusion limited erosion at all conditions considered due to their high combustion temperatures. Combined with reduced oxidizer concentrations – and possibly due to increased $H_2$ concentrations (Jones et al. 1986) – metallized propellants produced lower overall erosion rates than the non-metallized propellants. In the kinetically limited regime, rates increased exponentially with increasing temperatures, and nearly linearly with increasing pressures (i.e., increased heat transfer rates). Of the reaction mechanisms considered, the lowest predicted erosion rates were produced using Golovina’s kinetic parameters (Golovina 1980), while the greatest rates were produced by Libby’s parameters (Libby 1980; Libby and Blake 1981). With the combined results of these studies, it was determined that erosion rates are controlled by a combination of the heterogeneous reaction rates and gas-phase diffusion processes, of which Acharya and Kuo indicated a greater degree of uncertainty in the heterogeneous kinetics. This uncertainty was due to the low pressures at which most kinetics experiments were conducted in relation to rocket motor conditions, as well as discrepancies between correlations developed by different researchers.

In closely related studies, Thakre and Yang modeled graphite nozzle erosion at pressures between 6.9 and 45 MPa (1000 – 6000 psi) (Thakre and Yang 2008a; Thakre and Yang 2009b). These studies consider a single set of kinetic parameters assembled by Bradley et al. (Bradley et al. 1984). Using these kinetic rates, similar results to that of Acharya and Kuo were found. Water was found to be the most detrimental of all oxidizers, followed by $OH$ and $CO_2$; at very high temperatures and pressures, $OH$ was found at negligible concentrations and therefore could be neglected. As with the previous studies, metallized propellants created diffusion-limited erosion process due to the high temperatures created and lower oxidizer concentrations, leading to reduced overall erosion rates at pressures greater than 10 MPa. The transition from kinetically limited to diffusion limited recession was found to occur at surface temperatures of approximately 2800 K. It was
pointed out by both groups of researchers that surface temperatures are often greater than 2600 K, the temperature at which Geisler found substantial increases in erosion rates (Geisler 1981). Both groups also indicated that if increased heterogeneous reactions or decomposition of synthetic graphite occurs above this temperature, current knowledge of this process is not great enough to be accurately included in the models.

A.2 High Temperature Decomposition of Graphite

In order to address many of the concerns regarding high temperature decomposition of synthetic graphite, collaboration between several researchers (Prof. Kenneth Kuo, Prof. Richard Yetter, Dr. Ragini Acharya, Jonathan Essel, Justin Sabourin, and Dr. Jeffery Moore) at The Pennsylvania State University (PSU) began. The primary motivation for this work stemmed from a declaration made by Geisler, stating that increased erosion developed at temperatures greater than 2600 K occurs due to carbyne formation, a hypothesis arising from the work of Whittaker (Whittaker 1978). Whittaker explicitly stated in his work that carbon was unstable at temperatures above 2600 K at any pressure due to carbine formation (Fig. A-1).

Carbyne is a carbon allotrope with sp^1 electronic hybridization, creating linear carbon chains with alternating triple and single bonds (polyyne, [-C≡C-]_n) (Delhaes 2001). It is possible that the formation of these long chained carbon molecules may form, vaporize, and quickly decompose or react in the gas-phase. This vaporization process could potentially lead to increased nozzle erosion rates.

The formation and presence of carbyne at high temperatures is a topic of debate, particularly due to its instability, which is unquestioned (Whittaker 1978; Savvatimski 2005). There are clear results that indicate that linear carbon vapor chains can exist at high temperatures, and may be formed from a number of carbon sources (Mattauch et al. 1943; Heath et al. 1987; Weltner and Richard 1989; Orden and Saykally 1998).
Pure graphite is known to vaporize at 4098 K (sublimation point) under standard atmospheric conditions (Lide 2007). This temperature is much greater than the proposed carbyne formation temperature, and the shift in nozzle recession rates found by Geisler. Graphite nozzles are made from synthesized graphite. Synthetic graphite is made from several carbonaceous hydrocarbon materials, which are graphitized. During the manufacturing process much of the hydrogen and other impurities are removed, though a distinctly heterogeneous and slightly porous – depending on manufacturing procedures – solid remains (Tamashausky 2006). Preferential reaction (i.e., decomposition, oxidation, etc.) of the carbonaceous binder material may be a route that leads to increased erosion rates.

The following pages present the results of an experimental study conducted at PSU’s High Pressure Combustion Laboratory (HPCL) by Jonathan Essel and Justin Sabourin. The goal of this study was to explore the high temperature physical and chemical processes that take place with aerospace grade graphite in a non-oxidizing atmosphere. Several techniques were used to elucidate any mechanism(s) leading to the increased erosion found by Geisler and co-workers.
A.2.1 Experimental Approach

Using a high-power $CO_2$ laser (Coherent Everlase S48), high-density ($\rho = 1.9$ g/cm$^3$) aerospace grade graphite (G-90, Graphtek) was heated to temperatures in excess of 2800 K. The G-90 samples were machined into small diameter rods (3.2 mm by 4.7 mm long) using an EDM (electrical discharge machining). Nominal sample masses were approximately 0.055 g ($\pm 0.0025$ g). The bottom of the graphite samples also had a small recess drilled into them, allowing the sample to be mounted to the top of a hafnia ($HfO_2$) rod – diameter of 1.6 mm – in order to reduce conductive heat losses during laser heating. The hafnia rod also held up well to the high temperatures (melting point of approximately 3103 K).

In order to control heterogeneous reactions at the graphite surface, the sample was heated in a controlled atmosphere chamber (Fig. A-2). The Everlase $CO_2$ laser supplied a continuous wave of energy at powers up to 600 W. In order to increase the heat flux to the sample, the beam diameter was condensed and collimated with a pair of zinc selenide (ZnSe) lens (Design Research Optics). The beam was reduced by a factor of 2.5 from 16 mm down to 6.4 mm in diameter. Further details of this experimental setup may be found elsewhere (Essel et al. 2009).

Prior to testing, the controlled atmosphere chamber was evacuated to remove oxygen from the system before filling and purging the chamber with ultra high purity helium ($He$). Gases were delivered to chamber through two locations. The primary gas-delivery port, which was reserved for $He$ only, was located just below the $CO_2$ laser window – constructed of sodium chloride (NaCl). This primary intake cools the NaCl window, and keeps any vaporized species or particulates coming from the heated sample from contacting the window. The second gas intake delivers gases horizontally across the top of the heated sample surface, allowing for reactive gases such as $H_2$ to be delivered (Fig. A-3).
Figure A-2: Schematic of the graphite laser irradiation experiment, courtesy of: Jonathan Essel.

Figure A-3: Close-up schematic of laser-induced graphite ablation experiment, courtesy of: Jonathan Essel.
In all tests, system pressure was maintained at 0.31 MPa (45 psia), and samples were irradiated at varying applied heat fluxes *(i.e., laser powers)* for a time period of 30 sec. Flow rates were controlled to maintain consistency between tests, and the cross-flow gases were either *He* or *H₂*. Upper surface temperatures of the graphite were monitored using a three-color pyrometer (660, 750, and 850 nm). Emitted radiation was collected from a small spatial region at the center of the sample, and split into three separate fiber-optic cables, which coupled to photo-multiplier tubes (PMTs; Model H8249-102, Hamamatsu) containing different bandpass filters (Model 10BPF10, Newport Corporation). Using the method described by Khan *et al.* (Khan *et al.* 1990), which uses Wien’s radiative displacement law, ratios of radiative intensity were used to calculate surface temperatures. Calibration of the pyrometer was done using a standardized temperature source, which was a tungsten ribbon filament lamp (The Pyrometer Instrument Company, Inc.). Calibration curves were generated using the approach used by Goroshin *et al.* (Goroshin *et al.* 2006).

In addition to measuring the surface temperatures due to the applied heat flux, videos of the irradiation process were taken (Fig. A-4), and sample masses were carefully recorded before and after irradiation. A gas-sampling system was also implemented. Gases introduced through the cross-flow tube were collected after flowing across the top of the heated sample using a quartz sampling probe, connected to an air-actuated remotely controlled 10 port valve (Valco). This valve was programmed to sample gases near the heated surface for a 20 sec period, starting 5 sec after the onset of irradiation. Sampled gases were sent through an in-line nanoparticle filter, collecting condensed-phase species, before being captured in a Tedlar gas sampling bag. Subsequent chemical analysis of the captured gases was done using a gas chromatograph (GC-17A, Shimadzu), which used a flame ionization detector (FID) and a thermal conductivity detector (TCD). Unknown product gases were identified by comparing their elution times with the elution times of known standard gases in the same column type and with the same heating and flow conditions (Essel *et al.* 2009).
A.2.2 Experimental Results, Conclusions, and Significance

Results and conclusions of the laser ablation study stem from information gathered from several areas, including: 1) mass loss measurements, 2) video images of the heated sample and the ablated material plume, 3) surface temperatures, 4) microscopy of the synthetic graphite before and after irradiation, as well as collected condensed phase particles, 5) concentrations of gas-phase products, and 6) visual observations of the collected condensed-phase product quantities. Table A-1 provides a summary of these results. Graphical representations of the mass loss as functions of surface temperatures and laser power are shown in Fig. A-5.
The results shown in Table A-1 and Fig. A-5 illustrate that the mass losses are found at temperatures as low as ~2100 K, but losses increase substantially at temperatures approaching 2700 K. The surface temperature also appeared to be limited to 2700 K as well, and was not further increased with increasing heat fluxes. Mass loss rates did continue to increase exponentially with increasing laser power. Combined, these observations imply an endothermic phase transformation was taking place. The temperature at which this occurs is

### Table A-1: Summary of graphite laser irradiation tests.

<table>
<thead>
<tr>
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<tr>
<td></td>
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<tr>
<td>12</td>
<td>100</td>
<td>2042±202</td>
<td>2000±92</td>
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<td>He</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>14</td>
<td>125</td>
<td>2149±147</td>
<td>2119±74</td>
<td>0.6</td>
<td>He</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>13</td>
<td>150</td>
<td>2105±156</td>
<td>2090±81</td>
<td>0.5</td>
<td>He</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>01</td>
<td>250</td>
<td>2616±66</td>
<td>2626±42</td>
<td>0.7</td>
<td>He</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>02</td>
<td>300</td>
<td>2708±66</td>
<td>2646±42</td>
<td>0.9</td>
<td>He</td>
<td>5.4</td>
<td>0.0</td>
</tr>
<tr>
<td>03</td>
<td>350</td>
<td>2695±75</td>
<td>2645±55</td>
<td>2.1</td>
<td>He</td>
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<td>04</td>
<td>400</td>
<td>2687±87</td>
<td>2588±65</td>
<td>Contamination*</td>
<td>He</td>
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<td>3.6</td>
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<td>10</td>
<td>150</td>
<td>2456±83</td>
<td>2391±50</td>
<td>Contamination*</td>
<td>H₂</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>09</td>
<td>200</td>
<td>2411±79</td>
<td>2408±47</td>
<td>0.3</td>
<td>H₂</td>
<td>8.8</td>
<td>0.0</td>
</tr>
<tr>
<td>05</td>
<td>250</td>
<td>2528±95</td>
<td>2477±56</td>
<td>0.3</td>
<td>H₂</td>
<td>2.4</td>
<td>0.0</td>
</tr>
<tr>
<td>06</td>
<td>300</td>
<td>2625±89</td>
<td>2665±58</td>
<td>0.9</td>
<td>H₂</td>
<td>11.9</td>
<td>5.2</td>
</tr>
<tr>
<td>11</td>
<td>300</td>
<td>2659±50</td>
<td>2667±34</td>
<td>1.2</td>
<td>H₂</td>
<td>9.0</td>
<td>6.9</td>
</tr>
<tr>
<td>08</td>
<td>325</td>
<td>2677±65</td>
<td>2678±40</td>
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<td>H₂</td>
<td>17.1</td>
<td>120.9</td>
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<tr>
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<td>2709±75</td>
<td>2677±55</td>
<td>2.3</td>
<td>H₂</td>
<td>20.7</td>
<td>395.1</td>
</tr>
</tbody>
</table>

*contamination caused by melting of hafnia rod, which coated some of the graphite sample.

Figure A-5: Surface temperatures, laser power, and mass loss dependencies – comparison between H₂ and He cross-flow gases, courtesy of Jonathan Essel.

The results shown in Table A-1 and Fig. A-5 illustrate that the mass losses are found at temperatures as low as ~2100 K, but losses increase substantially at temperatures approaching 2700 K. The surface temperature also appeared to be limited to 2700 K as well, and was not further increased with increasing heat fluxes. Mass loss rates did continue to increase exponentially with increasing laser power. Combined, these observations imply an endothermic phase transformation was taking place. The temperature at which this occurs is
close to the predicted temperature of Geisler at which graphite nozzle erosion increases substantially, indicating the same mechanism is taking place in both experiments. The fact that $H_2$ and $He$ cross-flow gases do not alter the kinetics of this process meant that the erosion mechanism was due to synthetic graphite phase transformation at the surface as opposed to heterogeneous oxidation or reduction reactions. It should be noted that the G-90 manufacturer has indicated a thermal instability of this material at a temperature of 2873 K. This instability was not elaborated upon by the manufacturer, given the proximity of this temperature to the plateau temperature in Fig. A-5, it is likely that both thermal instabilities were caused by the same mechanism.

Although the results suggest that the induced mass loss was not due to a heterogeneous reaction, they did indicate that $H_2$ was highly reactive with the ablated carbon material. Table A-1 shows that in cases where $H_2$ was used as the cross-flow gas, notably larger concentrations of methane ($CH_4$) and acetylene ($C_2H_2$) were found. Additionally, the ablative plume that is clearly shown in Fig. A-4 was not seen in any of the videos when using $H_2$. The visible ablative plume was due to condensed phase particles emitting visible radiation. These particles were collected in the nanoparticle filter and examined using a scanning electron microscope (SEM, see Fig. A-6). Since a condensed-phase ablative plume was not formed when using $H_2$ as the cross-flow gas, no particles were collected in the filters. A visually dramatic difference in the two systems was found due to this effect (see Fig. A-7; also illustrated is the increased mass loss with increasing laser power).
Closer examination of the video images and measured gas concentrations provides insight into the chemical processes involved when $H_2$ was introduced. In Fig. A-4 a clear dark zone is depicted between the nozzle surface and the visible ablative plume. This dark zone, which was present to varying degrees in all $He$ cross-flow tests, indicated there were no solid particles present. It was determined that the synthetic graphite decomposes, forming a carbon vapor, which can be in several forms. In the $He$ system, the ablated carbon vapor condensed, forming soot-like particles, whereas when $H_2$ was present, the carbon vapor reacted to form gas-phase hydrocarbons – mainly $CH_4$ and $C_2H_2$ – instead of soot. The exact form of the carbon vapor is unknown. It is quite possible that carbyne-like species were formed, though spectroscopic studies would be required to confirm this.

These results clearly indicate that at temperatures greater than $2650 – 2700$ K a new chemical erosion process can occur, even in diffusion limited reaction regimes. More work is required to explore the relative importance of this mechanism compared to oxidation kinetics, though the work from Geisler indicates that this mechanism needs to be better understood so that it may be numerically modeled and mitigated in the future.
A.3 High Temperature Oxidation of Graphite

As discussed previously, the high temperature oxidation of graphite is an important but disruptive process in many applications. In most high temperature applications, oxidizers of interest are $O_2$, $CO_2$, $H_2O$, and $OH$. Unfortunately, there is a significant disparity between many of the kinetic correlations developed to describe these processes. The goal of the work presented here was to help resolve some of the questions relating to $H_2O$ and $CO_2$ oxidation. Previously developed correlations have used a modified form of the Arrhenius rate correlation (Eq. A-4), and assume $CO$ as the oxidation product (Table A-2).

$$\text{reaction rate} = A \cdot T^\beta \cdot \exp\left(\frac{-E_a}{R_u \cdot T}\right) \cdot \left(P_{\text{oxidizer}}\right)^n$$  \hspace{1cm} (A-4)
The results shown in the table above illustrate several discrepancies involving carbon-based material oxidation kinetics. Several publications indicate that $H_2O$ and $CO_2$ produce identical oxidation rates and activation energies (Golovina 1980; Libby 1980; Libby and Blake 1981; Culbertson and Brezinsky 2009). The kinetic mechanism of these systems is up for debate, though these kinetics would indicate that the formation or desorption of $CO(s)$ is the limiting reaction. Closer examination of the studies that found identical kinetics for $CO_2$ and $H_2O$ indicate little agreement regarding overall kinetics. Oxidation rates vary by as much as an order of magnitude, with varying reaction orders (i.e., pressure dependence).

Another study indicated that $CO_2$ and $H_2O$ have very different oxidation kinetics, but nearly identical activation energies (Bonneta
t and Hoynant 1965; Bradley et al. 1984). Each study presented in Table A-2 used different materials. In the work from Culbertson and Brezinsky (Culbertson and Brezinsky 2009), carbon black particles were used; however, subsequent testing used graphite flakes, producing identical reaction rates as the carbon black when the results are normalized by surface area (Brezinsky 2010). Therefore, it is expected that most forms of bulk carbon materials will exhibit similar reaction rates.

<table>
<thead>
<tr>
<th>Oxidizer</th>
<th>Kinetic Parameters</th>
<th>Reference(s)</th>
</tr>
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</table>
| $H_2O$           | $4.8 \times 10^4$ grams cm$^{-2}$ s$^{-1}$ atm$^{-0.5}$ | 0.0 68.8 0.5 (Bonneta
t and Hoynant 1965; Bradley et al. 1984) |
| $CO_2$           | 900 grams cm$^{-2}$ s$^{-1}$ atm$^{-0.5}$ | 0.0 68.1 0.5 (Bonneta
t and Hoynant 1965; Bradley et al. 1984) |
| $H_2O$ or $CO_2$| 247 grams cm$^{-2}$ s$^{-1}$ atm$^{-0.5}$ | 0.0 41.9 1.0 (Libby 1980; Libby and Blake 1981) |
| $H_2O$ or $CO_2$| 15.8 grams cm$^{-2}$ s$^{-1}$ atm$^{-0.5}$ | 0.0 40 1.0 (Golovina 1980) |
| $H_2O$ or $CO_2$| 61.1 grams cm$^{-2}$ s$^{-1}$ atm$^{-0.5}$ | 0.0 41 0.5 (Culbertson and Brezinsky 2009) |
| $O_2$            | 8710 grams cm$^{-2}$ s$^{-1}$ atm$^{-0.5}$ | 0.0 35.7 1.0 (Libby and Blake 1981) |
| $O$              | 66.55 grams K$^{0.5}$ cm$^{-2}$ s$^{-1}$ atm$^{-0.5}$ | -0.5 0.0 1.0 (Rosner and Allendorf 1968) |
| $OH$             | 36.5 grams K$^{0.5}$ cm$^{-2}$ s$^{-1}$ atm$^{-0.5}$ | -0.5 0.0 1.0 (Neoh et al. 1981) |

The results shown in the table above illustrate several discrepancies involving carbon-based material oxidation kinetics. Several publications indicate that $H_2O$ and $CO_2$ produce identical oxidation rates and activation energies (Golovina 1980; Libby 1980; Libby and Blake 1981; Culbertson and Brezinsky 2009). The kinetic mechanism of these systems is up for debate, though these kinetics would indicate that the formation or desorption of $CO(s)$ is the limiting reaction. Closer examination of the studies that found identical kinetics for $CO_2$ and $H_2O$ indicate little agreement regarding overall kinetics. Oxidation rates vary by as much as an order of magnitude, with varying reaction orders (i.e., pressure dependence).

Another study indicated that $CO_2$ and $H_2O$ have very different oxidation kinetics, but nearly identical activation energies (Bonneta
t and Hoynant 1965; Bradley et al. 1984). Each study presented in Table A-2 used different materials. In the work from Culbertson and Brezinsky (Culbertson and Brezinsky 2009), carbon black particles were used; however, subsequent testing used graphite flakes, producing identical reaction rates as the carbon black when the results are normalized by surface area (Brezinsky 2010). Therefore, it is expected that most forms of bulk carbon materials will exhibit similar reaction rates.
A.3.1 Carbon Dioxide and Water Vapor Oxidation Kinetics

The following experimental study used the same thermogravimetric (TG) flow reactor presented in Chapter 3 (3.1) to explore $H_2O$ and $CO_2$ oxidation rates with two types of synthetic graphite materials. The first type of graphite was GR001CC (Graphitek, $\rho = 1.81\text{ g/cm}^3$), while the second was aerospace grade G-90 (Pyrotek, $\rho = 1.9\text{ g/cm}^3$). The goals of these series of experiments were to: 1) determine any kinetic differences between the two different grades of graphite, 2) determine if $CO_2$ and $H_2O$ exhibit the same reaction rates, 3) determine if $H_2O$ and $CO_2$ rates are additive, 4) develop kinetic correlations and compare rates with previous studies, and 5) examine changes in surface morphology during oxidation. Changes in surface structure were characterized using SEM and BET analysis techniques.

A.3.1.1 Experimental Evaluation and Results

One of the goals of this study was to determine the differences in dissimilar grades of synthetic graphite. Initially TG and DSC studies were done during a transient heating process using an $O_2$ (20%) and argon atmosphere, employing a high precision commercially available thermal analyzer (Model STA 449C Jupiter, Netzsch GmbH). Results of these analyses, shown in Fig. A-8, do not suggest a substantial difference in the grades of graphite beyond density. Both produce essentially an equivalent amount of total heat release – evaluated by measuring the area under the DSC curves – and both begin to react at the same temperature. GR001CC graphite appears to react slightly faster than the G-90 grade, and also left a small amount of residue after testing; this suggests that the lower grade graphite has somewhat greater porosity during oxidation (since surface area is proportional to reaction rate), contains impurities, or is made of a more reactive carbon allotrope. Energy-dispersive X-ray spectroscopy (EDS) was performed along with SEM over several of the field of views shown in Fig. A-9, other than small quantities of calcium ($Ca$) in the GR001CC graphite, no other impurities were found. The presence of the $Ca$ may explain the left over residue and dynamic heat release shown in the thermal analysis of the GR001CC graphite (see Fig. A-8).
Using the large scale TG flow reactor developed as part of this dissertation, a single partial pressure of $H_2O$ and $CO_2$ was used for comparing the materials’ oxidation rates. All testing was done at a total reactor flow rate of 12 slpm. Due to pore formation – increasing oxidizer transport distances – and a large “fuming” effect found during graphite oxidation, diffusion limited reactions were found at lower temperatures than in the tungsten oxidation experiments, as noted by the curve in the data shown in Fig. A-10. Diffusion limited reactions became prevalent at lower temperature with the less dense GR001CC material than G-90 due to the larger concentration of pores produced (see Fig. A-9). The formation of pores reduces the gas diffusion coefficient – increasing time scales for diffusion of a gas molecule to a surface within a pore – as described by Knudsen pore diffusivity (see Appendix C).
Figure A-9: SEM images of synthetic graphite, before and after oxidation.
When evaluating the oxidation rates of GR001CC and G-90 graphite in $H_2O$ and $CO_2$ atmospheres at constant oxidizer partial pressures of 22.8 torr (0.03 atm) we can see that rates involving both oxidizing species and graphite types are nearly the same (Fig. A-11). The rates of GR001CC oxidation by $H_2O$ are indicated to be slightly greater than the rest. However, these rates have been corrected to account for changes in surface area during testing. It was determined that GR001CC and G-90 exhibit vastly different surface areas after oxidation. This is clearly seen in the SEM images of Fig. A-9.

Figure A-10: Graphite (GR001CC) and $H_2O$ oxidation rates in the flow reactor.
Surface homogeneity changes during oxidation were just one aspect of the synthetic graphite that was found to provide a significant variance from other materials such as tungsten. The surface structure of “as machined” graphite not only changes with oxidation time (i.e., mass loss), but is dependent on material type and oxidizing species. The SEM images illustrate the difference in the as machined sample and the post-test oxidized sample. During oxidation pores were formed at the graphite surface, which gradually grow into each other, leaving a rough and porous structure behind (Breval et al. 2002). The morphology and kinetics of this process can be altered by several mechanisms. From an experimental perspective this creates several issues. During TG flow reactor studies, the structure – specific surface area – is unknown during testing. To account for this, BET surface area measurements were conducted on the pre- and post-test samples. Using this information, as well as the measured planar area, it was determined that the surface area increases significantly during oxidation. In the case of GR001CC, surface areas may increase by as much as a factor of 9, while G-90 increases by approximately a factor of 2. The pore
formation and surface roughening process was estimated to occur during the initial oxidation process of the sample, before reaching a fairly steady-state roughness. This was determined by oxidizing an as machined sample for an extended period of time – mass loss rates initially increased rapidly before leveling off. This effect was viewed with all samples, regardless of graphite type or oxidizing species. However, changes in surface area were more reproducible with the G-90 graphite. All data presented in the figures have been corrected to account for the increased surface area due to oxidation. In the case of G-90, it was assumed that the surface area grows by a factor of 2, over approximately the initial 100 mg of the samples’ mass loss. In the cases of GR001CC, a factor of 6 was used. Typical sample dimensions for both graphite materials were 8.6 mm by 26 mm by 1 mm. In the future, a detailed study should be conducted to provide of better quantitative understanding of surface area changes of synthetic graphite as functions of reaction time, temperature, and oxidizing species.

Accounting for the effects of surface area, the data derived using the TG flow reactor from the different types of graphite nearly collapsed onto each other (see Fig. A-11). If the data were not normalized by the surface area, mass loss rates were much greater with the GR001CC graphite. The higher density material produced slower overall mass loss, but this was primarily due to the fact that the surface did not become porous during oxidation. The higher density material also indicated a slightly greater $E_a$; both materials designated a greater $E_a$ process for the CO$_2$ reaction compared to the H$_2$O reaction. The curve-fitted activation energies for G-90 were determined to be 55 and 61 kcal/mol for H$_2$O and CO$_2$, respectively, while GR001CC produced activation energies of 48 and 53 kcal/mol for H$_2$O and CO$_2$, respectively.

Even with the small differences in activation energies, with both types of synthetic graphite H$_2$O and CO$_2$ oxidation rates were nearly the same. This supports several previous studies that concluded that the kinetics of both oxidizers may be described using the same correlation with good accuracy. This suggests that there is a common limiting reaction between the two oxidizers. The limiting reaction could be either desorption of CO from the surface, or the formation of a transition state CO$_{(s)}$, which allows for subsequent desorption to occur. In both cases, dissociative adsorption of CO$_2$ (→CO + O$_{(s)}$) and H$_2$O (→H$_2$ + O$_{(s)}$) would be a fast and exothermic process that does not limit corrosion rates.
Discrepancies in several of the previous correlations developed were the oxidation rates’ oxidizer pressure dependencies. Some have indicated that an oxidizer pressure exponent of 1.0 describes the kinetics better, while others indicate 0.5. Independently, an appropriate value was determined using a series of tests conducted at constant temperature using the G-90 material (see 3.1.5 for rate analysis procedures). Both CO\textsubscript{2} and H\textsubscript{2}O oxidizers were considered at varying partial pressures, in both cases a pressure exponent of 0.5 was determined to provide a good description of the pressure dependence (Fig. A-12).

![Figure A-12: H\textsubscript{2}O and CO\textsubscript{2} pressure dependence of G-90 graphite oxidation reaction.](image)

Using the data presented in Fig. A-11 and Fig. A-12, four correlations were developed to estimate graphite oxidation kinetics of G-90 and GR001CC graphite materials in the presence of H\textsubscript{2}O and CO\textsubscript{2} at high temperatures. Each correlation was developed using a curve fitted exponential function to the data in Fig. A-11. These curve fitted correlations were then modified to conform to the Arrhenius correlation presented in Eq. 3-2, assuming a pressure exponent of 0.5. G-90 oxidation rates may be estimated using Eq. A-5 and Eq. A-6 for H\textsubscript{2}O and CO\textsubscript{2} oxidation, respectively, while GR001CC oxidation may be estimated using Eq. A-7 and Eq. A-8 for H\textsubscript{2}O and CO\textsubscript{2}, respectively.
Using the newly developed correlations for G-90 graphite oxidation, which are close to that of GR001CC when normalized by the surface area, a visual comparison was drawn with the correlations from previous researchers (see Fig. A-13). At both oxidizer partial pressures considered, the equated values from this study lie within the

\[
\dot{r}_{G-90-H_2O} = 85.2 \cdot \exp\left(\frac{-55.4 \text{kcal mol}^{-1}}{R \cdot T}\right) \left(P_{H_2O,\text{torr}}\right)^{0.5}
\]  
(A-5)

\[
\dot{r}_{G-90-CO_2} = 852 \cdot \exp\left(\frac{-61.2 \text{kcal mol}^{-1}}{R \cdot T}\right) \left(P_{CO_2,\text{torr}}\right)^{0.5}
\]  
(A-6)

\[
\dot{r}_{GR001CC-H_2O} = 23.3 \cdot \exp\left(\frac{-48.2 \text{kcal mol}^{-1}}{R \cdot T}\right) \left(P_{H_2O,\text{torr}}\right)^{0.5}
\]  
(A-7)

\[
\dot{r}_{GR001CC-CO_2} = 62.8 \cdot \exp\left(\frac{-53.4 \text{kcal mol}^{-1}}{R \cdot T}\right) \left(P_{CO_2,\text{torr}}\right)^{0.5}
\]  
(A-8)

Figure A-13: Comparison of correlations developed to describe high temperature oxidation of carbon-based materials by \(CO_2\) and \(H_2O\), partial pressures of: (a) 25 torr and (b) 250 torr.
correlations. The slowest rates are predicted by the correlations from Golovina and Bradley et al. (Golovina 1980; Bradley et al. 1984), while the fastest rates are predicted by Culbertson and Brezinsky or Libby and Blake (Libby 1980; Libby and Blake 1981; Culbertson and Brezinsky 2009), except for the highest temperatures and lowest pressures, where the kinetics formulated in this dissertation are greatest. Due to the larger oxidizer pressure dependence, the correlation from Libby and Blake predicts the fastest rates at higher oxidizer partial pressures.

In addition to answering several questions regarding oxidation rates of different graphite materials and different oxidizing species, another goal of this work was to determine if the kinetics of multiple oxidizing species are additive. A mixture of CO$_2$ and H$_2$O was considered, each with a partial pressure of 11.2 torr or a total oxidizer partial pressure of 22.4 torr (Fig. A-14). The results seem to indicate that the mixtures of CO$_2$ and H$_2$O are not additive, but when combined produce lower than expected kinetics. It should be noted that there was excess H$_2$ in the system left over from the steam generator, however, this is a very small fraction of the total oxidizer partial pressure. In the future, if a scientist or engineer is

![Figure A-14: Rates of G-90 graphite oxidation by a mixture of H$_2$O and CO$_2$.](image-url)
to use an additive approach to predict oxidation rates of graphite in a mixture of $CO_2$ and $H_2O$, it should be expected that rates will be over-predicted.

A.3.1.2 Summary and Conclusions

A systematic study of the oxidation of two types of synthetic graphite was conducted. Results indicated that there is significant difference between the two types of graphite considered, although the surface area normalized kinetics were within experimental uncertainty of each other. The lower density graphite material, GR001CC, was found to contain small traces of calcium, and also became very porous during extended oxidation, increasing the surface area of the test samples by more than a factor of 5. By reason of this large increase in surface area, the lower density graphite lost mass due to heterogeneous oxidation reactions at a much greater rate than the higher density graphite. The higher density material, G-90, illustrated a similar surface roughening phenomena as the GR001CC graphite, but was not as porous. This caused G-90 surface areas to increase only about a factor of 2, and also allowed for kinetically limited reactions to be evaluated at much higher temperatures since pore diffusion was not as large of an issue.

Due to its use in high performance rocket motors, G-90 was evaluated in much greater detail than GR001CC. The oxidation rates of G-90 were similar to GR001CC when normalized by surface area, although activation energies of the kinetic processes were indicated to be slightly higher with G-90. Both materials revealed that $CO_2$ oxidation is a slightly higher activation energy process than $H_2O$ oxidation, but produce similar overall kinetics. The activation energies for G-90 were determined to be 55 and 61 kcal/mol for $H_2O$ and $CO_2$ oxidation, respectively. Additionally, the oxidation rate oxidizer pressure dependence was determined to be 0.5 for both $CO_2$ and $H_2O$. The correlations derived from the data of this study match well with those previously reported, although the activation energies were higher than the majority. Results indicated that $CO_2$ and $H_2O$ oxidation rates are not additive, but the rates are inhibited when these species exist concurrently.
Appendix B

THERMODYNAMIC EQUILIBRIUM CALCULATIONS OF TUNGSTEN ROCKET NOZZLE OXIDATION

Thermodynamic equilibrium calculations were used to predict the major product species of tungsten rocket nozzle erosion, and compare these results with the flow reactor conditions of the TG flow reactor using NASA’s CEA software (McBride and Gordon 1996). Calculations assumed quasi-equilibrium conditions were obtained in the near surface region of the nozzle due to high temperatures yielding fast kinetics, and the primary reacting species to be pure tungsten, as would be the case in the control volume constraint in the nozzle boundary layer. Several well characterized propellant formulations were studied, including aluminized and non-aluminized composite propellants of ammonium perchlorate (AP, \(NH_4ClO_4\)), ammonium dinitramide \([ADN, NH_4N(NO_2)_2]\) and hydroxyl-terminated polybutadiene (HTPB, \(C_{10}H_{15.4}O_{0.07}\)), as shown in Table B-1. These formulations are not suggested as an actual propellant and rocket nozzle combination (in some cases they are impractical); however, the calculations provide useful insight into experimental design, and simple explanations of nozzle erosion mechanisms. In addition to the propellant formulations, the equilibrium combustion product mole fractions are presented at a single temperature and pressure. These results illustrate the oxidizing potential of the product mixture. The product species that have been identified as the primary oxidizers in rocket systems are highlighted in bold font. The results in Table B-1 also illustrate the large amount of \(CO\) and \(H_2\) formed during the solid propellant combustion process, particularly when using an aluminized propellant. These species have been identified as oxidation inhibitors (see 5.1.2.1 and 5.1.3.1). Although not shown, there are some pressure and temperature trends found in the propellant combustion product species. As temperatures increase, dissociation of the dominant oxidizers \((CO_2 \text{ and } H_2O)\) increases and radical species \((OH, NO, O)\) concentrations increase. Concentrations of the inhibiting species mentioned increase as a function of temperature under most conditions. Changes in species concentrations with temperature are subdued with increasing pressure, therefore the greatest changes in product concentrations are found under low pressure conditions.
The range of pressures considered were 14.7 to 3000 psia (0.10 – 20.68 MPa or 1 – 204 atm), while temperatures ranged from 1600 to 3400 K (2912 – 6152°F). Some of the calculated results of propellant A are shown in Fig. B-1 and Fig. B-2. Figure B-1 reports the equilibrium composition at four pressures: 14.7, 100, 1000, and 3000 psia. Under all conditions, except at the lowest pressures and highest temperatures, the dominant tungsten containing species were gaseous $WO_2Cl_2$ and $WO_2(OH)_2$. In fact, under the complete range of conditions, tungsten generally formed gaseous species and the primary erosion mechanism would appear to be a chemical oxidation process, free of condensed phase product species, therefore physical mechanisms of erosion can be neglected. It is known that rocket motors that use tungsten nozzles and non-aluminized AP-based propellants have significant problems with nozzle erosion. Even though this combination of propellant and nozzle is not practical, these equilibrium calculations provide a simple rationalization for the experimentally observed trends of excessive erosion due to the large amount of volatile compounds formed during oxidation. They also predict that the same species are present and in approximately the same relative proportions at atmospheric pressure as they are at high pressures. This result would seem to indicate that low pressure experiments should be able to yield the kinetics of interest in high pressure rocket nozzles.

<table>
<thead>
<tr>
<th>Propellant Designator</th>
<th>Propellant Formulation [wt%]</th>
<th>Equilibrium Product Mole Fractions at 100 psia (0.69 MPa) and 2800 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$CO = 0.110$ $CO_2 = 0.114$ $Cl = 0.016$ $HCl = 0.175$ $H_2 = 0.056$ $H_2O = 0.404$ $N_2 = 0.095$ $OH = 0.016$ $O_2 = 0.004$</td>
</tr>
<tr>
<td>A</td>
<td>88% AP and 12% HTPB</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$CO = 0.218$ $CO_2 = 0.011$ $Cl = 0.006$ $HCl = 0.152$ $H_2 = 0.307$ $H_2O = 0.107$ $N_2 = 0.080$ $OH = 0.002$ $O_2 = 0.000$ $Al_2O_3(L) = 0.097$</td>
</tr>
<tr>
<td>B</td>
<td>69% AP, 11.5% HTPB, and 19.5% Al</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$CO = 0.122$ $CO_2 = 0.069$ $H_2 = 0.094$ $H_2O = 0.369$ $N_2 = 0.321$ $OH = 0.012$ $O_2 = 0.001$</td>
</tr>
<tr>
<td>C</td>
<td>88.4% ADN and 11.6% HTPB</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$CO = 0.197$ $CO_2 = 0.006$ $H_2 = 0.352$ $H_2O = 0.069$ $N_2 = 0.269$ $OH = 0.001$ $O_2 = 0.000$ $Al_2O_3(L) = 0.087$</td>
</tr>
<tr>
<td>D</td>
<td>69% ADN, 11.5% HTPB, and 19.5% Al</td>
<td></td>
</tr>
</tbody>
</table>
Figure B-1: Equilibrium speciation in the boundary layer of a tungsten nozzle at pressures of 14.7, 100, 1000, and 3000 psia with propellant A.
In the another set of calculations with propellant A, it was assumed that the tungsten oxychloride and tungstic acid were kinetically limited and not formed in the boundary layer due to the larger number of bonds, requiring longer reaction times. These calculations are also representative of a hydrogen and chlorine free propellant since the only species containing Cl and H were removed. The results, presented in Fig. B-2 for pressures of 14.7, 100, 1000, and 3000 psia, show that the major product species range from completely gaseous oxides to multiple phases of oxides as a function of pressure and temperature.

Figure B-2: Equilibrium speciation in the boundary layer of a tungsten nozzle at pressures of 14.7, 100, 1000, and 3000 psia with propellant A – assuming no WO$_2$Cl$_2$ or WO$_2$(OH)$_2$ formation.
Although not shown, solid $WO_2$ formed at the lowest temperatures, *i.e.*, 1700 K and below. At atmospheric pressure, and temperatures greater than 1800 K, the products were entirely gaseous. This is much the same as when chlorine was present in the combustion gases. The dominant species were the trimer and dimer of tungsten trioxide. In the situation that these polymers are kinetically limited, the dominate species is expected to be $WO_3$. As the pressure increased (e.g., to 100 psia), liquid $WO_3$ was formed over a narrow temperature window (from about 1800 to 2000 K). As the pressure was further increased, the temperature window of liquid $WO_3$ – the primary tungsten oxide species – increased to temperatures as high as 3000 K at 1000 psia and to considerably higher temperatures at 3000 psia. This liquid could be envisioned to form on the tungsten nozzle surface, and hence physical erosion mechanisms in addition to chemical oxidation would be important. However, the equilibrium calculations did not restrict the liquid oxide formation to the surface and depending on the oxidation mechanism of tungsten suboxides, the liquid could equally form in the gas-phase within the boundary layer. It is interesting to note that halogens have a similar effect on the products of tungsten as they do with aluminum and boron combustion where condensed phase oxidation products at combustion temperatures are converted to oxychlorides (or oxyfluorides), which are generally gaseous products. In terms of detailed reaction analysis, the formation of liquid $WO_3$ may be important when trying to predict high pressure and temperature oxidation kinetics, particularly as an intermediate species.

Another set of equilibrium calculations used a composite aluminized propellant (propellant B) and a tungsten nozzle. Results of the dominant equilibrium tungsten oxide speciation over the range of temperatures considered are presented in Fig. B-3 at pressures of 14.7 and 3000 psia. As with the previous calculations of the non-aluminized propellant A, the dominant tungsten containing species were gaseous $WO_2Cl_2$ and $WO_2(OH)_2$, except for the highest temperature and lowest pressure conditions. Additionally, the primary species were the same and exist in the same relative proportions, which is why only two pressure conditions are shown in Fig. B-3. The addition of aluminum into the propellant reduced the relative amounts of all tungsten oxides in the boundary layer. Tungsten oxychloride ($WO_2Cl_2$) was reduced by approximately one order of magnitude while the other species were reduced even more, including $WO_2(OH)_2$. No liquid $WO_3$ was found over the entire
range of temperatures and pressures considered. However, there was liquid $Al_2O_3$ formed at temperatures above approximately 2300 K over the entire range of pressures. Below this temperature the $Al_2O_3$ solidified. Excluding the dominant chlorine and hydrogen containing species, under most conditions tungsten dioxide and trioxide were prominent species, with the exception being the dimer of tungsten trioxide at temperatures below approximately 1800 K. As the temperature was increased, $WO$ surpassed $(WO_3)_2$ and nearly reached the same mole fractions as $WO_2$ and $WO_3$. As with propellant A, the formation tungsten oxychloride and tungstic acid species were assumed to be kinetically limited and removed as possible species in the calculations. This yielded relatively the same results as in Fig. B-2, except for the emergence of liquid $WO_3$. It would appear that the aluminum presence has the same effect as including the dominate equilibrium species $[WO_2(OH)_2]$. Under all conditions, either liquid or solid $Al_2O_3$ was the dominant aluminum containing species, as shown in Fig. B-4. This species, which was a very large mole fraction of the combustion products, contains a large amount of the oxygen that may otherwise oxidize with the tungsten nozzle, increasing erosion. Although not shown, oxidation of aluminum to alumina by water vapor also produced a significant amount of $H_2$, which is shown in this dissertation to have significant oxidation inhibiting effects. Since alumina does
not include chlorine, this will occur with non-chlorine containing propellants as well. Although no intermetallic species containing $W$ and $Al$ were present in the thermodynamic database used, it was assumed that an insignificant amount of $Al$ reacts with the $W$ surface, though it is possible for $Al$ to react with tungsten oxides (see Eq. 2-23).

Figure B-4: Aluminum containing equilibrium species in the in boundary layer of a tungsten nozzle at pressures of 14.7, 100, 1000, and 3000 psia using propellant B.

In order to confirm some of the established general trends, a third set of calculations were performed with a second non-aluminized and aluminized propellant containing ADN, a non-chlorine containing compound. ADN was chosen only as an illustrative example of an energetic oxidizer – a positive oxygen balance (+25.8%) – with no chlorine. Using
propellant C, and the same temperature and pressure ranges as before, Fig. B-5 was derived, which presents the tungsten and oxygen containing species at pressures of 14.7 and 3000 psia. As expected, the results in Fig. B-5 are close to those of the propellant A speciation with the exception of $WO_2Cl_2$ formation. Over the entire range of pressures considered, no liquid $WO_3$ was formed, and tungstic acid was the dominate species, with the exception of the lowest pressures and highest temperatures considered. Increases in pressure led to greater amounts of the acid formation, reducing $WO_2$ and $WO_3$ formation. Elimination of $WO_2(OH)_2$ from equilibrium consideration created nearly the same results as shown in Fig. B-2; liquid $WO_3$ begins to appear as the dominate species in the equilibrium mole fractions, particularly at high pressures.

Figure B-5: Equilibrium mole fractions of tungsten and oxygen containing species in the boundary layer of a tungsten nozzle at pressures of 14.7 and 3000 psia using propellant C.

Although not shown, equilibrium calculations of propellant D yielded similar results as propellant B, excluding the chlorine containing species. The same tungsten oxides dominated, and existed in the same relative proportions. The dominant aluminum containing species was $Al_2O_3$ throughout. As shown in the prior calculations, liquid phase tungsten oxide was not found in the equilibrium products.

These thermodynamic equilibrium results have important implications with regards to erosion of tungsten-based nozzles, as well as to the design of fundamental kinetics experiments and interpretation of oxidation mechanisms. The results suggest that lower
pressures should be able to yield the kinetics of interest in high pressure nozzle erosion since the same speciation and relative amounts exist at lower pressures. The results also suggest which species will need to be considered in any elementary oxidation reaction mechanism to describe the chemical erosion process in environments with and without chlorine. Hydrogen is a component of nearly all advanced propellants, and therefore tungstic acid should be considered in nearly all chemical erosion mechanisms of tungsten based nozzles.

These results also illustrate how the erosion mechanism can change from one involving purely chemical oxidation and vaporization to one involving both physical and chemical mechanisms as a function of temperature, pressure, and propellant composition. The results of the equilibrium calculations advocate for the use of aluminized propellants in tungsten-based nozzles as chemical oxidation of tungsten was significantly reduced due to the strong affinity of oxygen for aluminum, reducing concentrations of oxidizers and increasing concentrations of $H_2$ and $CO$. This conclusion was previously reported by Opekka using the former mechanism (i.e., reduced oxidizer concentrations) though the use of similar calculations (Opekka 2004). The addition of aluminum also eliminated liquid $WO_3$ formation, which may reduce the physical erosion mechanism. However, liquid and solid $Al_2O_3$ are combustion products at high temperature and pressure, which may contribute to physical erosion through particle impact, and therefore the physical erosion mechanism cannot totally be neglected. However, the liquid $Al_2O_3$ may have an additional benefit in terms of reducing chemical erosion. It can be imagined that the liquid alumina would coat the nozzle surface, creating a physical barrier against the diffusion of gaseous oxidizing species to the bulk tungsten surface, thereby dramatically slowing oxidation rates. However, affects on nozzle performance are untold.
Appendix C

DIFFUSION LIMITED HETEROGENEOUS REACTIONS

As shown in Fig. 2-1, heterogeneous reactions can depend on several processes. Some of these processes lay beyond just the chemical reaction between two or more reactants of multiple phases. For a heterogeneous chemical reaction to occur the reactants must first come into contact with each other, which requires convective and diffusive movement of the reactants into close proximity. In some situations, particularly low temperature reactions, the time scale associated with this movement is much shorter than the time scale to complete a chemical reaction, producing a kinetically limited reaction. This means that the chemical reaction is the rate-controlling process, and reactions may not occur any faster without altering the chemical reaction mechanism. Often times the chemical reaction time scale is much faster than the time scale required to bring the reactants into close proximity with each other. Since diffusion is usually the primary mode of molecular transport, these slower reaction processes are called diffusion controlled or diffusion limited reactions. Diffusion limited reactions are generally prevalent under high temperature conditions, or in cases where diffusion must occur across a high density medium (e.g., gas-phase diffusion through a membrane or a metal-oxide passivation layer). In cases of diffusion limited reactions, mass transfer becomes more important for prediction of chemical rate processes than understanding of chemical kinetics themselves. This Appendix presents background for understanding diffusion, and methods for predicting diffusion limited heterogeneous reaction rates.

Diffusion is caused by random molecular motion that leads to complete mixing (Cussler 1997). Generally this process is described mathematically in engineering practices using the mass transfer coefficient, $k$ (Eq. C-1), which has units of length per unit time. Using this equation, the flux of gas-phase oxidizers may be determined per unit surface area. In the case of a heterogeneous oxidation reaction where diffusion limited reactions are anticipated, reaction rates may be estimated using Eq. C-1. However, this requires that some knowledge of the oxidation reaction stoichiometry be known, as well as the concentration of
oxidizing species \( (c_{ox}) \), surface geometry and morphology, as well as flow conditions of the gases surrounding the material being oxidized. The need to know the \( c_{ox} \) values is obvious from the equation; flow conditions and solid material geometry are needed to estimate the diffusion coefficient \( (D) \), and in turn the mass transfer coefficient.

\[
N_{ox} \left[ \frac{\text{flux}}{\text{surface area}} \right] = k \Delta c_{ox} \quad \text{(C-1)}
\]

### C.1 Gas-phase Diffusion Coefficients

Typical values for a diffusion coefficient are: 0.1 cm\(^2\)/s for gases, 10\(^{-5}\) cm\(^2\)/s for liquids, and 10\(^{-10}\) cm\(^2\)/s for solids. It is clear that liquid or solid oxidizer systems are much more likely to be diffusion limited than gas-phase oxidizers. Due to the nature of this dissertation, gas-phase oxidizing systems will only be considered. At approximately room temperature and atmospheric pressures, most studies have shown that diffusion coefficients exhibit a pressure dependence of \( P^{-1} \), and a temperature dependence of \( T^{1.5-1.8} \) (Cussler 1997). These dependencies are important in the interpretation of heterogeneous reaction rate data so that diffusion limited conditions may be identified.

On occasion, gas-phase mixtures, temperatures and pressures of interest to an engineer or scientist have been evaluated experimentally, and diffusion coefficients are known (Reid et al. 1977). However, more often estimations must be made using an appropriate correlation and/or theory. One of the more common theories used in this estimation is the Chapman-Enskog theory (Eq. C-2), which describes the diffusion coefficient for a two component mixture (Chapman and Cowling 1970). This theory is based on the analysis of molecular motion of gases, and assumes the gases are non-polar, which excludes the estimation of compounds like water. The pressure, \( P \), is defined in units of atmospheres. The quantities \( \sigma \) and \( \Omega \) are the collision diameter and the collision integral, respectively. The collision diameter is derived using Eq. C-3, assuming the gas-phase species are hard spheres; values for individual species can be found in tabular form in other sources (Hirschfelder et al. 1954; Cussler 1997).
The collision integral used in the Chapman-Enskog theory is, from a theoretical perspective, more complex than the collision diameter, but it is also tabulated and can be easily obtained (Hirschfelder et al. 1954; Cussler 1997). The use of these tables requires the calculation of Lennard-Jones potential interactions. The energy of interaction is a geometric average of the contributions from the two species, and is defined by Eq. C-4. As with the other values, individual species energies have been tabulated and can be found in numerous sources. Through practice, the Chapman-Enskog theory has been determined to be most often accurate to within 8% of true values.

\[ \sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \]  

(C-3)

Due to the inherent limitations placed on the Chapman-Enskog theory owed to its assumptions, many researchers have used numerous experimental studies to develop empirical correlations. A good representation of these efforts is presented in Eq. C-5 (Fuller et al. 1966), where \( V_{ij} \) are the volumes of parts of molecule \( j \), which are tabulated elsewhere (Fuller et al. 1966; Cussler 1997). This correlation has been shown to provide slightly better results than the previous theory. It is interesting to note that although the equation below was developed from experimental data, similar or identical pressure, temperature, and molecular weight dependencies were found as with Chapman-Enskog theory.

\[
D \left[ \frac{cm^2}{s} \right] = 1.86 \times 10^{-3} \cdot T^{3/2} \cdot \left( \frac{1}{MW_i} + \frac{1}{MW_j} \right)^{1/2} \frac{P \cdot \sigma_{ij}^2 \cdot \Omega}{\sum_i V_{i1}^{3/2} + \left( \sum_i V_{i2} \right)^{3/2}}
\]

(C-5)
C.1.1 High Pressure Conditions

Both of the previous theories were developed to predict diffusion coefficients of dilute gas mixtures under low pressure conditions. For this reason their accuracy diminishes with increasing pressure. To combat this, several approaches may be taken to improve the estimation’s accuracy. These approaches would be particularly important for estimation of diffusion coefficients at rocket motor conditions. At higher pressures, a simple density corrected approach can be taken (see Eq. C-6), as suggested by Reid et al. (Reid et al. 1977). This high pressure correction for the diffusion coefficient assumes the same temperature for both pressure conditions, and should also be used with caution near the critical point.

\[ D_{\text{high } p} = \rho_{\text{high } p} \cdot (\rho D)_{\text{low } p} \]  \hspace{1cm} (C-6)

Another correction has been derived by Takahashi (Takahashi 1974). Takahashi’s correlation relates a high pressure correction factor to the reduced pressure and temperature of the system, of which were empirically determined within Takahashi’s work.

C.1.2 Pore Diffusion

In addition to high pressure conditions, diffusion into pores can also vastly affect diffusion coefficients, and in turn diffusion limited heterogeneous reaction rates. The schematic in Fig. C-1 shows how much more complex the pore diffusion process is compared to the regular diffusion process. The diffusion into the pore is difficult due to the small opening of the pore; additionally, if heterogeneous reactions occur there may be gases concurrently trying to diffuse out of the pore, slowing the overall mass transfer process. The Knudsen pore diffusion coefficient was developed to quantitatively describe the pore diffusion process of species \( i \) (Eq. C-7), where \( r \) is the pore radius in centimeters (Satterfield and Sherwood 1963; Culbertson and Brezinsky 2009).

\[ D_{K,i}[cm/s] = 9700 \cdot r \sqrt{T/MW_i} \]  \hspace{1cm} (C-7)
If the system pressure is sufficiently low, the entire diffusion process may be controlled by pore diffusion, since Knudsen pore diffusion is independent of pressure as opposed to inversely dependent. Likewise, at high pressures pore diffusion may not be important. The combined transport resistances can be used to create a net diffusivity coefficient using Eq. C-8, where the first term is the pore diffusion resistance, and the second term is the diffusive resistance estimated using Eq. C-2 or Eq. C-5.

\[
D_{\text{eff}} = \left( \frac{1}{D_{K,i}} + \frac{1}{D} \right)
\]  
(C-8)

C.2 Mass Transfer Correlations

In many systems of interest to engineers and scientists, mass transfer coefficients are of primary interest in order to predict how chemical processes will behave. This is especially true of heterogeneous reaction systems. Estimation of mass transfer coefficients, which is very often done using modified correlations developed to predict heat transfer rates, requires knowledge of fluid dynamic properties of the gases, as well as geometry of the solid interface. Several of the correlations that are most useful to this dissertation, as well as correlations that may be of interest in other heterogeneous oxidation processes are shown in Table C-1. Many of the correlations use dimensionless groups, specifically the Reynolds number and the Schmidt number. The Reynolds number describes the fluid dynamic flow conditions, specifically the ratio of inertial forces to viscous forces (see Eq. C-9, where \( l \) is...
the characteristic length and may be a diameter of a sphere, the length of a plate, or some other length). The Schmidt number, a less common dimensionless parameter, is defined as the ratio of momentum diffusivity to mass diffusivity (Eq. C-10), and therefore is inversely proportional to the diffusion coefficient.

\[ \text{Re}_l = \frac{\rho v}{\mu} \]  
(C-9)

\[ Sc = \frac{\mu}{\rho D} \]  
(C-10)

Table C-1: Select mass-transfer correlations for fluid-solid interfaces.

<table>
<thead>
<tr>
<th>Physical Situation</th>
<th>Correlation</th>
<th>Key Variables / Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laminar flow along flat plate ( ^a )</td>
<td>( \frac{kL}{D} = 0.646 \left( \text{Re}_l \right)^{1/2} \left( \text{Sc} \right)^{1/4} )</td>
<td>Re(_l) defined using plate length and bulk gas velocity</td>
</tr>
<tr>
<td>Forced convection around solid sphere</td>
<td>( \frac{kd}{D} = 2.0 + 0.6 \left( \text{Re}_d \right)^{1/2} \left( \text{Sc} \right)^{1/4} )</td>
<td>Re(_d) defined using sphere diameter and velocity of sphere</td>
</tr>
<tr>
<td>Laminar flow through circular tube</td>
<td>( \frac{kd}{D} = 1.62 \left( \frac{d^3 v_{ave}}{LD} \right)^{1/4} )</td>
<td>( L ) is the pipe length; ( d ) is the pipe diameter; ( v_{ave} ) is the average velocity in tube</td>
</tr>
<tr>
<td>Turbulent flow through circular tube</td>
<td>( \frac{kd}{D} = 0.026 \left( \text{Re}_d \right)^{1/3} \left( \text{Sc} \right)^{1/3} )</td>
<td>Re(_d) defined using pipe diameter and the average velocity in tube</td>
</tr>
<tr>
<td>Packed beds</td>
<td>( \frac{k}{v_{ave}} = 1.17 \left( \text{Re}_d \right)^{0.8} \left( \frac{D}{v} \right)^{2/3} )</td>
<td>Re(_d) defined using particle diameter and the superficial velocity through the bed</td>
</tr>
</tbody>
</table>

\( ^a \) mass transfer coefficient averaged over length \( L \). \(*\)adapted from: (Cussler 1997).

With estimation of the diffusion coefficient from C.1, and knowledge of the flow conditions, approximation of the mass transfer coefficient is straightforward. Along with comprehension of the stoichiometry of a heterogeneous oxidation reaction, diffusion limited reaction rates can be predicted. For instance, the TG flow reactor used in this study can be considered as laminar flow over a flat plate. To determine the mass transfer coefficient, the Reynolds number must be determined along with the Schmidt number and the diffusion coefficient. In the case of \( O_2 \) oxidation the Chapman-Enskog theory may be used since \( O_2 \) is non-polar, however, for \( CO_2 \) and \( H_2O \) Eq. C-5 should be used to estimate \( D \). In the case of tungsten oxidation, it may be assumed that \( WO_3 \) is the primary desorption species over a wide range of conditions, therefore three \( O_2 \) molecules are required to reach the surface to
remove two tungsten atoms. In that case, the diffusion limited tungsten mass loss rate would be two-thirds of the diffusive mass flux. With this analysis it becomes apparent why a clear understanding of the reaction stoichiometry is extremely important in diffusion limited reaction rate estimations.
This code implements the model discussed within this dissertation to solve for tungsten oxidation and corrosion rates as a function of several reactor variables, including temperature and oxidizer concentrations. The code was written in FORTRAN 77 (Etter 1990) and compiled for use on Microsoft Windows using Compaq Visual Fortran 6.5.0. Libraries from CHEMKIN-III were also used. Details regarding subroutines used from this library, as well as code indexes/pointers may be found in the appropriate manuals (Coltrin et al. 1996; Kee et al. 1996).

The following is the application or flow reactor program (see Fig. 4-4), which contains governing equations, specific parameter calculations, as well as control of input and output files:

```fortran
C******************************************************************************
PROGRAM WOXIDATION
C
C This program has been developed from the Chemkin-III sksamp.f program
C as well as a program developed by Zhe Wang at Penn State. Dr. Wang's
C program was developed to model (1D,open) iron carburization kinetics,
C which is similar to a deposition process. This program models a
C similar geometry, however high temperature tungsten oxidation is
C modeled, which leads to bulk tungsten material loss.
C
C*****precision > double
IMPLICIT DOUBLE PRECISION (A-H,O-Z), INTEGER(I-N)
C*****END precision > double
C
PARAMETER (LENIWK=40000, LENRWK=1000000, LENCWK=300, LINCK=46,
1 LINSK=36, NLMAX=65, LIN=5, LOUT=6, KMAX=100,
2 MAXP=20, ITOL=1, IOPT=0, ITASK=1,
3 RTOL=1.0E-15, ATOL=1.E-30)
C
DIMENSION Z(KMAX), IWORK(LENIWK), RWORK(LENRWK), X(KMAX),
1 WT_GASIN(10)
DIMENSION SDOTI(50), SITDTI(5)
DIMENSION ROP(50),WO3flux(50),WO2flux(50),WO2sflux(50)
C
COMMON /RPAR/T, P, VOL_REACTOR, AREA_SURF, GASIN(10), FLOWIN,
1 WT_MIX_IN
COMMON /IPAR/KKGAS, KKSURF, KKBULK, KKTOT, NFSURF, NLSURF,
1 NFBULK, NLBLK, NISK, NIPKK, NIPKF, NIPKL,
2 NRSK, NSDEN, NSCOV, NX, NWDOT, NWT, NACT,
3 NSDOT, NSITDT, INDEXGAS, IGASIN(10)
CHARACTER*16 CWORK(LENCWK), KSYM(KMAX), PNAM(MAXP)
```
CHARACTER*80 LINE
C
LOGICAL KERR, IERR
EXTERNAL FUN, CKTIME
DATA KERR/.FALSE./, KSYM/KMAX*' '/, PNAM/MAXP*' '/, ZERO/0.0/
C
TSTART = CKTIME (ZERO)
C
Open the CHEMKIN and SURFACE LINK files
C
C*****linkfile (gas) > binary
OPEN (LINCK,FORM='UNFORMATTED', STATUS='UNKNOWN',FILE='chem.bin')
C*****END linkfile (gas) > binary
C*****linkfile (surface) > binary
OPEN (LINSK,FORM='UNFORMATTED', STATUS='UNKNOWN',
     FILE='surfWox.bin')
C*****END linkfile (surface) > binary
C
Open program input and output files
C
OPEN (LIN,FORM='FORMATTED', STATUS='UNKNOWN',FILE='Input_Wox.inp')
OPEN (LOUT,FORM='FORMATTED', STATUS='UNKNOWN',
     FILE='Output_Wox.out')
C
Open additional files for output
C
OPEN (9,FORM='FORMATTED', STATUS='UNKNOWN',FILE='bulkWloss.txt')
WRITE(9,*) '    Time(sec)    ',' moles_W/(cm^2-sec)'
OPEN (10,FORM='FORMATTED', STATUS='UNKNOWN',FILE='gas.txt')
OPEN (11,FORM='FORMATTED', STATUS='UNKNOWN',FILE='surface.txt')
OPEN (12,FORM='FORMATTED', STATUS='UNKNOWN',FILE='WO3_flux.txt')
OPEN (13,FORM='FORMATTED', STATUS='UNKNOWN',FILE='WO2_flux.txt')
OPEN (14,FORM='FORMATTED', STATUS='UNKNOWN',FILE='WO2s_flux.txt')
OPEN (15,FORM='FORMATTED', STATUS='UNKNOWN',
     FILE='Total_DesorptionRates.txt')
WRITE(15,*) '    Time(sec)    ','moles_WO3/(cm^2-sec)',
             'moles_WO2/(cm^2-sec)', 'moles_O/(cm^2-sec)'
C
****************************************************************************
C Beginning of program initialization
****************************************************************************
C
Find lengths necessary for arrays
C
CALL CKLEN (LINCK, LOUT, LENI, LENR, LENC, IFLAG1)
CALL SKLEN (LINSK, LOUT, LENIS, LENRS, LENC, IFLAG2)
C
IF (IFLAG1.GT.0 .OR. IFLAG2.GT.0) THEN
WRITE (LOUT, *)
1   'STOP...ERROR INITIALIZING LINKFILES...'
STOP
ENDIF
C
LITOT = LENI + LENIS
LRTOT = LENR + LENRS
LCTOT = MAX(LENC, LENCS)
IF (LITOT.GT.LENIWK .OR. LRTOT.GT.LENRWK .OR. LCTOT.GT.LENCWK) THEN
   IF (LITOT.GT.LENIWK) WRITE (LOUT, *)
1      ' Error...LENIWK must be at least ', LITOT
   IF (LRTOT.GT.LENRWK) WRITE (LOUT, *)
1      ' Error...LENRWK must be at least ', LRTOT
   IF (LCTOT.GT.LENCWK) WRITE (LOUT, *)
1      ' Error...LENCWK must be at least ', LCTOT
STOP
ENDF

C
C Initialize CHEMKIN and SURFACE arrays
C
CALL CKINIT (LENI, LENR, LENC, LINCK, LOUT, IWORK, RWORK, 1  CWORK, IFLAG)
IF (IFLAG .GT. 0) THEN
  WRITE (LOUT, *) 1
  STOP...ERROR INITIALIZING CHEMKIN WORKSPACE...
ENDIF
CALL CKINDX (IWORK, RWORK, MM, KKGAS, II, NFIT)

C
NISK = LENI + 1
NRSK = LENR + 1
CALL SKINIT (LENIS, LENRS, LENCS, LINSK, LOUT, IWORK(NISK), 1  RWORK(NRSK), CWORK, IFLAG)
IF (IFLAG .GT. 0) THEN
  WRITE (LOUT, *) 1
  STOP...ERROR INITIALIZING SURFACE WORKSPACE...
ENDIF
CALL SKINDX (IWORK(NISK), NELEM, KKGAS, KKSUR, KKBULK, KKTOT, 1  NNPHAS, NNSURF,
2  NPSURF, NLSURF, NFBULK, NLBULK, IISUR)

C
NIPKK = NISK  + LENIS
NIPKF = NIPKK + NNPHAS
NIPKL = NIPKF + NNPHAS
NICOV = NIPKL + NNPHAS
NEQ  = KKTOT + 1 + NNSURF
NIODE = NICOV + KKTOT
LIW   = 30 + NEQ
ITOT  = NIODE + LIW - 1

C
NSDEN = NRSK + LENRS
NSCOV = NSDEN + NNPHAS
NX    = NSCOV + KKTOT
NWDOT = NX    + KKTOT
NWT   = NWDOT + KKGAS
NACT  = NWT   + KKTOT
NSDOT = NACT  + KKTOT
NSITDT= NSDOT + KKTOT
NRODE = NSITDT + NNPHAS
LRW   = 22 + 9*NEQ + 2*NEQ**2
NTOT  = NRODE + LRW - 1

C
IF (LENIWK.LT.ITOT .OR. LENRWK.LT.NTOT .OR. KMAX.LT.KKTOT 1  .OR. MAXP.LT.NNPHAS) THEN
  IF (LENIWK .LT. ITOT) WRITE (LOUT, *)
  ' Error...LENIWK too small...must be at least ', ITOT
  IF (LENRWK .LT. NTOT) WRITE (LOUT, *)
  ' Error...LENRWK too small...must be at least ', NTOT
  IF (KMAX .LT. KKTOT) WRITE (LOUT, *)
  ' Error...KMAX too small...must be at least ', KKTOT
  IF (MAXP .LT. NNPHAS) WRITE (LOUT, *)
  ' Error...MAXP too small...must be at least ', NNPHAS
  STOP
ENDIF

C
C Create phase pointers. NIPKF are 1st species in each phase, and
NIPKL are the last species in each phase.

CALL SKPKK (IWORK(NISK), IWORK(NIPK), IWORK(NIPK),
               1     IWORK(NIPKL))

Create real array of site densities starting with NSDEN
CALL SKSDEN (IWORK(NISK), RWORK(NRSK), RWORK(NSDEN))

Create integer array of site coverage numbers
CALL SKCOV (IWORK(NISK), IWORK(NICOV))

Create real array from integer array of site occupancies.
Set real array (NX to NX+KKTOT) equal to zero, which is used to store
initial mole fractions.
DO 30 K = 1, KKTOT
   RWORK(NRCOV + K - 1) = IWORK(NICOV + K - 1)
   RWORK(NX + K - 1) = 0.0
30 CONTINUE

Create character string array of species names.
CALL SKSYMS (IWORK(NISK), CWORK, LOUT, KSYM, IERR)
KERR = KERR.OR.IERR

Create character string array of phase names
CALL SKSYMP (IWORK(NISK), CWORK, LOUT, PNAM, IERR)
KERR = KERR.OR.IERR

Create real array of species molecular weights
CALL SKWT (IWORK(NISK), RWORK(NRSK), RWORK(NWT))

Create values for universal gas constant and pressure.
RU is in egs, PATM is pressure of 1 atm in cgs units (see manual).
CALL SKRP (IWORK(NISK), RWORK(NRSK), RU, RUC, PATM)

IF (KERR) THEN
   WRITE (LOUT, *)
   1   'STOP...ERROR INITIALIZING CONSTANTS...'
   STOP
ENDIF

*****************************************************************************
C Begin reading and printing of initial conditions
*****************************************************************************

Pressure and temperature

WRITE (LOUT, '(/A)')
  1    ' INPUT INITIAL PRESSURE(ATM) AND TEMPERATURE(K)'
READ (LIN, *) PA, T
WRITE (LOUT,7105) PA, T

Convert pressure to cgs units
P = PA*PATM

Reactor Volume

WRITE (LOUT, '(/A)') ' INPUT VOLUME OF REACTION ZONE (cm^3)'
READ (LIN,*) VOL_REACTOR
WRITE (LOUT,7105) VOL_REACTOR

Reactor Flow Rate

WRITE (LOUT, '(/A)') ' INPUT FLOWRATE INTO REACTOR (SLPM)'
READ (LIN,*) FLOWIN_SLPM
WRITE (LOUT,7105) FLOWIN_SLPM

Read/Print Tungsten Surface Area

WRITE (LOUT, '(/A)') ' INPUT SURFACE AREA OF BULK TUNGSTEN (cm^2)'

STOP...ERROR INITIALIZING CONSTANTS...
READ (LIN,*) AREA_SURF
WRITE (LOUT,7105) AREA_SURF

INDEXGAS = 0

Read/Print Initial non-zero moles (stored NX to NX+KKTOT in work array)
Initial non-zero moles

40 CONTINUE
LINE = ' '
WRITE (LOUT, '(/A)') ' INPUT INITIAL ACTIVITY OF NEXT SPECIES'
READ (LIN, '(A)', END=45) LINE
ILEN = INDEX (LINE, '!')
IF (ILEN .EQ. 1) GO TO 40

ILEN = ILEN - 1
IF (ILEN .LE. 0) ILEN = LEN(LINE)
IF (INDEX(LINE(1:ILEN), 'END') .EQ. 0) THEN
   IF (LINE(1:ILEN) .NE. ' ') THEN
      CALL SKSNUM (LINE(1:ILEN), 1, LOUT, KSYM, KKTOT, PNAM,
                   NNPHAS, IWORK(NIPKK), KNUM, NKF, NVAL,
                   VAL, IERR)
      IF (IERR) THEN
         WRITE (LOUT,*) ' Error reading moles...' KERR = .TRUE.
      ELSE
         RWORK(NX + KNUM - 1) = VAL
      ENDIF
   ENDIF
ENDIF
GO TO 40
ENDIF

FLOWIN = FLOWIN_SLPM / 22.4 / 60.0
WT_MIX_IN = 0.0
DO 42 K = 1,INDEXGAS
   WT_MIX_IN = WT_MIX_IN + WT_GASIN(K)
42 CONTINUE

45 CONTINUE
IF (KERR) THEN
   WRITE (LOUT, '*') 'STOP...ERROR INITIALIZING USER INPUT...
   STOP
ENDIF

Final time and print interval
WRITE (LOUT, '(/A)') ' INPUT FINAL TIME AND DT'
READ (LIN, *) T2, DT
WRITE (LOUT,7105) T2, DT

Normalize the mole fractions for each phase
DO 60 N = 1, NNPHAS
XTOT = 0.0
KFIRST = IWORK(NIPKF + N - 1)
KLAST = IWORK(NIPKL + N - 1)
DO 50 K = KFIRST, KLAST
   XTOT = XTOT + RWORK(NX + K - 1)
50 CONTINUE
IF (XTOT .NE. 0.0) THEN
   DO 55 K = KFIRST, KLAST
      RWORK(NX + K - 1) = RWORK(NX + K - 1) / XTOT
55 CONTINUE
ELSE
   WRITE (LOUT, *) ' ERROR...NO SPECIES WERE INPUT FOR PHASE ' // PNAM(N)
   KERR = .TRUE.
ENDIF
60 CONTINUE
IF (KERR) THEN
   WRITE (LOUT, *) 'STOP...ERROR INITIALIZING SOLUTION...'
   STOP
ENDIF
C
C     Initial conditions
C
TT1  = 0.0
C     Initial gas-phase mass fractions
CALL CKXTY (RWORK(NX), IWORK, RWORK, Z)
C     Initial surface site fractions
KFIRST = IWORK(NIPKF + NFSURF - 1)
KLAST  = IWORK(NIPKL + NLSURF - 1)
DO 110 K = KFIRST, KLAST
   Z(K) = RWORK(NX + K - 1)
110 CONTINUE
C     Initial bulk deposit amounts
C In this program tungsten is the only bulk species
KFIRST = IWORK(NIPKF + NFBULK - 1)
Z(KFIRST) = 0.5
120 CONTINUE
C     Initial gas-phase mass density (stored as Z(KKTOT+1)
CALL CKRHOY (P, T, Z, IWORK, RWORK, Z(KKTOT+1) )
C     Initial surface site densities
DO 130 N = NFSURF, NLSURF
   Z(KKTOT+1+N-NFSURF+1) = RWORK(NSDEN + N - 1)
130 CONTINUE
C
C     Integration control parameters for LSODE
C
TT2   = TT1
C     MF = 22 uses a stiff, internal Jacobian method
MF    = 22
ISTATE= 1
C
C***********************************************************************
C     Integration loop for solution of problem
C***********************************************************************
C
250 CONTINUE
C
C     Print the solution
C
C Computer pressure (P) of system given mass density.
CALL CKPY  (Z(KKTOT+1), T, Z(1), IWORK, RWORK, P)
WRITE (LOUT,*) ' ', TT2
WRITE (LOUT, 7100) P, T, Z(KKTOT+1)
WRITE (LOUT, *) ' GAS-PHASE MOLE FRACTIONS'
CALL CKYTX (Z, IWORK, RWORK, RWORK(NX))
CALL PRT1 (KKGAS, KSYM, LOUT, RWORK(NX))

DO 190 N = NFSURF, NLSURF
   WRITE (LOUT, *) ' SURFACE SITE FRACTIONS ON PHASE (SITE) ', N
   KKPHAS = IWORK(NIPKK + N - 1)
   KFIRST = IWORK(NIPKF + N - 1)
   CALL PRT1 (KKPHAS, KSYM(KFIRST), LOUT, Z(KFIRST))

   SUM = 0.0
   KFIRST = IWORK(NIPKF + N - 1)
   KLAST = IWORK(NIPKL + N - 1)
   DO 185 K = KFIRST, KLAST
      SUM = SUM + Z(K)
   185 CONTINUE
   WRITE (LOUT,*)'  SUM OF SURFACE SITE FRACTIONS', SUM
   WRITE (LOUT,*)'  SURFACE SITE DENSITY  ', Z(KKTOT+1+N-NFSURF+1)
190 CONTINUE

KFIRST = IWORK(NIPKF + NFBULK -1)

C**********************************************************Add outputs here for graphing data
C
CALL CKYTX (Z, IWORK, RWORK, X)
SDOTW = RWORK(NSDOT + KKTOT - 1)
WRITE(LOUT,*) ' ' WRITE(LOUT,*) ' BULK W REMOVAL = ', SDOTW, ' moles W / cm^2-sec'
C Print to tungsten removal rate file
WRITE(9, 7116) TT2, SDOTW
C Print to gas phase mole fraction file
WRITE(10, 7116) TT2, (X(K), K=1,KKGAS)
C Print to surface phase surface coverage file
KFIRST = IWORK(NIPKF + NFSURF -1)
KLAST = IWORK(NIPKL + NFSURF -1)
WRITE(11, 7116) TT2, (Z(K), K=KFIRST,KLAST)

C
CALL SKROP  (P, T, RWORK(NACT), RWORK(NSDEN),
            IWORK(NISK), RWORK(NRSK), ROP)

DO 195 IR=1,IISUR
   CALL SKRATI  (IR, ROP, IWORK(NISK), RWORK(NRSK), SDOTI, SITDI)
   WO3flux(IR)= SDOTI(KKGAS)
   WO2flux(IR)= SDOTI(KKGAS-1)
   WO2sflux(IR)= SDOTI(KKGAS+2)
195 CONTINUE

C
CALL SKRATI  (8, ROP, IWORK(NISK), RWORK(NRSK), SDOTI, SITDI)
SDOTO = SDOTI(KKGAS-3)

SDOTWO2 = RWORK(NSDOT + KKGAS - 2)
SDOTWO3 = RWORK(NSDOT + KKGAS - 1)

C Writes files of desorption rates of WO2, WO3, and O
WRITE(12, 7116) TT2, (WO3flux(K), K=1,IISUR)
WRITE(13, 7116) TT2, (WO2flux(K), K=1,IISUR)
WRITE(14, 7116) TT2, (WO2sflux(K), K=1,IISUR)
WRITE(15, 7116) TT2, SDOTWO3, SDOTWO2, SDOTO
IF (TT2 .GE. T2) THEN  
  WRITE (OUT, *) 'STOP...TIME LIMIT REACHED...'  
SECS = CKTIME (TSTART)  
  IF (SECS .GT. 60) THEN  
    WRITE (OUT, *) ' Total CPUtime (min): ',SECS/60  
  ELSE  
    WRITE (OUT, *) ' Total CPUtime (sec): ',SECS  
  ENDIF  
  STOP  
ENDIF  
C  
C Alter time steps depending on time of reaction  
C  
C IF(TT2.GT.10000) DT = 100.0  
C IF(TT2.LE.10000) DT = 1.0  
IF(TT2.LE.10) DT = 1  
IF(TT2.LE.5) DT = 0.5  
IF(TT2.LE.1) DT = 1E-3  
IF(TT2.LE.0.1) DT = 1E-4  
IF(TT2.LE.0.001) DT = 1E-6  
IF(TT2.LE.0.00001) DT = 1E-8  
C  
TT2 = MIN(TT2 + DT, T2)  
C  
C Call the differential equation solver  
C  
350 CONTINUE  
C****precision > double  
CALL DVOODE  
C****END precision > double  
* (FUN, NEQ, Z, TT1, TT2, ITOL, RTOL, ATOL, ITASK,  
  1 ISTATE, IOPT, RWORK(NRODE), LRW, IWORK(NIODE),  
  2 LIW, JAC, MF, RWORK, IWORK)  
C  
IF (ISTATE .LE. -1) THEN  
  IF (ISTATE .EQ. -1) THEN  
    ISTATE = 2  
    GO TO 350  
  ELSE  
    WRITE (OUT,*) 'ERROR, ISTATE=',ISTATE  
    STOP  
  ENDIF  
ENDIF  
C  
C Return to the beginning of the solution loop  
GO TO 250  
CLOSE(9)  
CLOSE(10)  
CLOSE(11)  
CLOSE(12)  
CLOSE(13)  
CLOSE(14)  
CLOSE(15)  
C  
7003 FORMAT (1H1)  
7100 FORMAT (1H , ' GAS-PHASE STATE', /,  
  1 ' P = ', 1PE12.4, ' T = ', 1PE12.4, ' DENSITY = ', 1PE12.4)  
7105 FORMAT (12E11.3)  
7110 FORMAT (26X, 5(1X,A10))  
7115 FORMAT (22X, 10E11.3)  
7116 FORMAT (E18.10,1X,25(E18.10,1X))
SUBROUTINE FUN (NEQ, TIME, Z, ZP, RWORK, IWORK)

C*****precision > double
IMPLICIT DOUBLE PRECISION(A-H,O-Z), INTEGER(I-N)
C*****END precision > double

DIMENSION Z(NEQ), ZP(NEQ), RWORK(*), IWORK(*)

COMMON /RPAR/T, P, VOL_REACTOR, AREA_SURF, GASIN(10), FLOWIN, 1
WT_MIX_IN
COMMON /IPAR/KKGAS, KKSURF, KKBULK, KKTOT, NFSURF, NLSURF, 1
NFBULK, NLBULK, NISK, NIPKK, NIPKF, NIPKL, 2
NRSK, NSDEN, NRCOV, NX, NWDOT, NWT, NACT, 3
NSDOT, NSITDT, INDEXGAS, IGASIN(10)

Variables in Z are:  Z(K) = Y(K), K=1,KKGAS
Z(K) = SURFACE SITE FRACTIONS,  
    K=KFIRST(NFSURF), KLAST(NLSURF)
Z(K) = BULK SPECIES MASS,  
    K=KFIRST(NFBULK), KLAST(NLBULK)
Z(K) = GAS-PHASE MASS DENSITY, K=KKTOT+1
Z(K) = SURFACE SITE MOLAR DENSITIES,  
    K=KKTOT+2, KKTOT+1+NNSURF

Call CHEMKIN and SURFACE CHEMKIN subroutines

Calculate pressure of system
CALL CKPY  (Z(KKTOT+1), T, Z(1), IWORK, RWORK, P)
Calculate molar production rates of species given P, T, and 
mass fractions (Z).
CALL CKWYP (P, T, Z(1), IWORK, RWORK, RWORK(NWDOT))
Calculate mole fractions (i.e. activity)
CALL CKYTX (Z, IWORK, RWORK, RWORK(NACT))

KFIRST = IWORK(NIPKF + NFSURF - 1)
KLAST = IWORK(NIPKL + NLSURF - 1)
DO 100 K = KFIRST, KLAST
   RWORK(NACT + K - 1) = Z(K)
100 CONTINUE

KFIRST = IWORK(NIPKF + NFBULK - 1)
KLAST = IWORK(NIPKL + NLBULK - 1)
DO 150 K = KFIRST, KLAST
   RWORK(NACT + K - 1) = RWORK(NX + K - 1)
150 CONTINUE

DO 175 N = NFSURF, NSURF  
   RWORK(NSDEN + N - 1) = Z(KKTOT+1+N-NFSURF+1)
175 CONTINUE

CALL SKRAT (P, T, RWORK(NACT), RWORK(NSDEN), IWORK(NISK), 1
   RWORK(NRSK), RWORK(NSDOT), RWORK(NSITDT))
Form mass density equation

** PRINT*, FLOWIN

DELTA_FLOW = 0.0
DO 200 K = 1, KKGAS
  WDOT = RWORK(NWDOT + K - 1)
  SDOT = RWORK(NSDOT + K - 1)
  DELTA_FLOW = DELTA_FLOW + WDOT*VOL_REACTOR + SDOT*AREA_SURF
200 CONTINUE

** PRINT*, DELTA_FLOW

Molecular flow out of system (mols/sec)
FLOWOUT = DELTA_FLOW + FLOWIN
** PRINT*, FLOWOUT

WT_MIX = 0.0
DO 210 K = 1, KKGAS
  WT = RWORK(NWT + K - 1)
  WT_MIX = WT_MIX + WT * RWORK(NACT + K - 1)
210 CONTINUE

** PRINT*, WT_MIX

FLOWOUT_MASS = WT_MIX * FLOWOUT
** PRINT*, FLOWOUT_MASS

FLOWIN_MASS = WT_MIX_IN * FLOWIN
** PRINT*, FLOWIN_MASS

SUM = 0.0
DO 240 K = 1, KKGAS
  SDOT = RWORK(NSDOT + K - 1)
  WT = RWORK(NWT + K - 1)
  SUM = SUM + (AREA_SURF * WT * SDOT / VOL_REACTOR)
240 CONTINUE

ZP(KKTOT+1) = (FLOWIN_MASS - FLOWOUT_MASS) / VOL_REACTOR + SUM
** PRINT*, ZP(KKTOT+1)

Form the gas-phase mass conservation equation

DO 300 K = 1, KKGAS
  WDOT = RWORK(NWDOT + K - 1)
  WT = RWORK(NWT + K - 1)
  SDOT = RWORK(NSDOT + K - 1)
  FLOWIN_TEMP = 0.0
  DO 250 I = 1, INDEXGAS
    IF(K.EQ.IGASIN(I)) FLOWIN_TEMP = GASIN(I) * WT
 250 CONTINUE

ZP(K) = ( - Z(K) * ZP(KKTOT+1) + WDOT * WT
 1 + (AREA_SURF / VOL_REACTOR) * SDOT * WT +
 2 (FLOWIN TEMP - Z(K) * FLOWOUT_MASS) / VOL_REACTOR )
 3 / Z(KKTOT+1)
300 CONTINUE

Form the surface mass equations

DO 400 N = NFSURF, NLSURF
  SITDOT = RWORK(NSITDT + N - 1)
Below is the input file to the gas-phase mechanism interpreter – the gas-phase chemistry/thermochemistry input (see Fig. 4-4). The mechanisms were taken from the same source (Li et al. 2004; Li et al. 2007), whom assembled these mechanisms from several other
studies. The few thermodynamic inputs involving tungsten species were added by the dissertation author.

This Cl mechanism is based on the CH3OH mechanism of Held and Dryer (IJCK, 1998, 30, 805) with following important revision:

1. H2/O2 subset is updated to that of Li et al. (IJCK, in press, 2004)
2. CO + OH = CO2 + H is optimized to fit the literature experimental result
3. HCO + M = H + CO + M is optimized to fit the literature experimental result
4. CH3 + H2O = CH3O + OH is modified to match Scire's value at 1000 K
5. CH3 + HO2 = CH4 + H is taken from Scire (IJCK, 2001, 33, 75)
6. CH3 + O2 = CH2O + OH is taken from Scire (2002, Ph.D. thesis)
7. CH2O + HO2 = HCO + H2O2 is from Elteneer et al. (JPC A, 1998, 102, 5196)
8. CH2O + H = HCO + H2 is taken from Irdam et al. (IJCK 1993, 25, 285)
9. CH2O + M reactions are from Friedrichs et al.(IJCK 2004, 36, 157)
10. CH3OH decomposition reactions are taken from GRI-3.0 (1999)
11. CH2O + H = CH2 + H2O is taken from Friedrichs et al. (IJCK, 2004, 36, 157)
12. CH2O + H = CH3O + CO is changed to keep the branching ratio with the above reaction
13. HCOOH reactions are not included since it is not important and has large uncertainties
14. dHf of OH is adjusted to 8.91 kcal/mol (Ruscic et al. JPC A. 2002, 106, 2727)
15. thermochemical data of CH2O is fit to Johnson & Hudgens' table (JPC 1996, 100, 19874)

11/2/2008, JLS: Elements, species and reactions not needed for W-oxidation model removed
11/2/2008, JLS: Thermo for WO2, WO3 added from CEA data (taken from JANNAF tables)

ELEMENTS
O He W C H

SPECIES
O2 CO
CO2 H2O
H2O2
H OH
HO2 O

THERMO ALL
0300.00 1000.00 5000.00
H2O L 5/89H 10 2 0 0 0G 200.000 3500.000 1000.000 1
4.01721090E+00 2.239892013E-03 6.336681506E-07 1.142265708E-10 1.079805935E-14 2
1.118567313E+02 3.78510215E+00 4.30179801E+00 4.74912051E-03 2.11582991E-05 3
-2.42763949E-08 9.29225124E-12 2.94808040E+02 3.71666245E+00 1.04026120E+04 4
AR 120186AR 1 G 0300.00 5000.00 1000.00 1
0.02500000E+02 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 2
-0.07453750E+04 0.04366001E+02 0.02500000E+02 0.00000000E+00 0.00000000E+00 3
0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 4
CO 121286C 10 1 G 0300.00 5000.00 1000.00 1
0.02500000E+02 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 2
-0.07453750E+04 0.04366001E+02 0.02500000E+02 0.00000000E+00 0.00000000E+00 3
0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 4
H2 121286C 10 1 G 0300.00 5000.00 1000.00 1
0.02500000E+02 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 2
-0.07453750E+04 0.04366001E+02 0.02500000E+02 0.00000000E+00 0.00000000E+00 3
0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 4
REATIONS

No gas phase reaction available for tungsten oxides, all mechanisms from Li.

END

\[ \text{O} + \text{O} + \text{M} = \text{O}_2 + \text{M} \]
\[ k = 6.165 \times 10^{15}, \quad \Delta H = -0.50, \quad \Delta S = 0.00 \]

H2/2.5/ H2O/12/


\[ \text{O} + \text{O} + \text{AR} = \text{O}_2 + \text{AR} \]
\[ k = 1.886 \times 10^{13}, \quad \Delta H = 0.00, \quad \Delta S = -1.788 \times 10^{3} \]

H2/2.5/ H2O/12/


\[ \text{O} + \text{H} + \text{M} = \text{OH} + \text{M} \]
\[ k = 4.714 \times 10^{18}, \quad \Delta H = -1.00, \quad \Delta S = 0.00 \]

H2/2.5/ H2O/12/


\[ \text{H} + \text{OH} + \text{M} = \text{H}_2 + \text{O}_2 + \text{M} \]
\[ k = 2.212 \times 10^{22}, \quad \Delta H = -2.00, \quad \Delta S = 5.248 \times 10^{2} \]

H2/2.5/ H2O/12/


\[ \text{H} + \text{OH} + \text{M} = \text{H}_2 + \text{O}_2 + \text{M} \]
\[ k = 3.8 \times 10^{22}, \quad \Delta H = -2.00, \quad \Delta S = 0.00 \]

H2/2.5/ H2O/12/


\[ \text{HO}_2 + \text{H} = \text{H}_2 + \text{O}_2 \]
\[ k = 1.66 \times 10^{13}, \quad \Delta H = 0.00, \quad \Delta S = 8.23 \times 10^{3} \]

H2/2.5/ H2O/12/


\[ \text{HO}_2 + \text{OH} = \text{H}_2\text{O}_2 + \text{OH} \]
\[ k = 7.079 \times 10^{13}, \quad \Delta H = 0.00, \quad \Delta S = 2.95 \times 10^{3} \]

H2/2.5/ H2O/12/


\[ \text{HO}_2 + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H} \]
\[ k = 4.2 \times 10^{14}, \quad \Delta H = 1.182 \times 10^{4}, \quad \Delta S = -1.629 \times 10^{3} \]

H2/2.5/ H2O/12/


\[ \text{HO}_2 + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H} \]
\[ k = 1.3 \times 10^{11}, \quad \Delta H = -1.629 \times 10^{3} \]

H2/2.5/ H2O/12/
The following illustrates a sample input file to the surface mechanism interpreter – the surface- and bulk-phase chemistry and thermochemical input (see Fig. 4-4). Notice that all thermodynamic parameters are the same. These parameters were mostly unknown. Therefore, reversible chemical processes were purposefully not used in the mechanisms. Only in cases where reversible reactions were used were true thermodynamic parameters needed.
THERMO ALL

300.  1000.  2000.

W(b)   W  1.  0.  0.  0.S  1000.000  3200.000  2600.000  1
2.79908468E+00  4.91696607E-04  2.39387045E-08  5.73869058E-13  13-2.29258422E-16  2
-8.58170165E+02  1.21715994E+01  1.11873583E+02  1.65628577E-01  1.65628577E-01  8.1626701E-05  3
2.05817926E-08  1.7569319E-12  6.24041303E+04  6.57738071E+02  4

W(s)   W  1.  0.  0.  0.S  1000.000  3200.000  2600.000  1
2.79908468E+00  4.91696607E-04  2.39387045E-08  5.73869058E-13  13-2.29258422E-16  2
-8.58170165E+02  1.21715994E+01  1.11873583E+02  1.65628577E-01  1.65628577E-01  8.1626701E-05  3
2.05817926E-08  1.7569319E-12  6.24041303E+04  6.57738071E+02  4

WO(s)  O  1.W  1.  0.  0.S  1000.000  3200.000  2600.000  1
2.79908468E+00  4.91696607E-04  2.39387045E-08  5.73869058E-13  13-2.29258422E-16  2
-8.58170165E+02  1.21715994E+01  1.11873583E+02  1.65628577E-01  1.65628577E-01  8.1626701E-05  3
2.05817926E-08  1.7569319E-12  6.24041303E+04  6.57738071E+02  4

WO2(s) O  2.W  1.  0.  0.S  1000.000  3200.000  2600.000  1
2.79908468E+00  4.91696607E-04  2.39387045E-08  5.73869058E-13  13-2.29258422E-16  2
-8.58170165E+02  1.21715994E+01  1.11873583E+02  1.65628577E-01  1.65628577E-01  8.1626701E-05  3
2.05817926E-08  1.7569319E-12  6.24041303E+04  6.57738071E+02  4

WO3(s) O  3.W  1.  0.  0.S  1000.000  3200.000  2600.000  1
2.79908468E+00  4.91696607E-04  2.39387045E-08  5.73869058E-13  13-2.29258422E-16  2
-8.58170165E+02  1.21715994E+01  1.11873583E+02  1.65628577E-01  1.65628577E-01  8.1626701E-05  3
2.05817926E-08  1.7569319E-12  6.24041303E+04  6.57738071E+02  4

END

REACTIONS kcal/mole

2W(s)+O2=>2WO(s)  1.40E+21  0.5  0.0
2WO(s)+O2=>2WO2(s)  1.40E+21  0.5  0.0
W(s)+O=>WO(s)  1.93E+12  0.5  0.0
WO(s)+O=>WO2(s)  1.93E+12  0.5  0.0
WO2(s)+O=>WO3(s)  1.93E+12  0.5  0.0
2WO2(s)+O2=>2WO3(s)  1.44E+21  0.5  26.0
2WO3(s)=>2WO2(s)+O2  2.20E+19  1.0  3.0
WO3(s)+WO(s)=>2WO2(s)  1.00E+23  0.0  1.0
2WO2(s)=>WO3(s)+WO(s)  1.00E+23  0.0  74.5
WO2(s)+W(s)=>2WO(s)  1.00E+23  0.0  3.0
2WO3(s)+W(s)=>W(s)  1.00E+23  0.0  35.0
WO2(s)+O=WO(s)  2.08E+10  1.0  126.5
WO3(s)+O=WO2(s)  2.08E+10  1.0  53.0
W(b)+2WO3(s)=>WO3+WO2(s)+WO(s)  2.21E+19  1.0  1.0
W(b)+2WO3(s)=>WO2+2WO2(s)  2.21E+19  1.0  2.0
W(b)+WO2(s)+WO3(s)=>WO3+2WO(s)  2.21E+19  1.0  47.5
W(b)+WO2(s)+WO3(s)=>WO2+WO(s)+WO2(s)  2.21E+19  1.0  73.8
W(b)+WO3(s)=>WO3+W(s)  2.08E+10  1.0  79.5
W(b)+WO3(s)=>WO2+WO(s)  2.08E+10  1.0  73.8

END
Justin L. Sabourin was born in Rutland, Vermont on March 3, 1981. He was raised in the Rutland area and attended Mill River Union High School in nearby North Clarendon, VT. After high school he decided to attend Union College in Schenectady, New York due to its strong academic reputation and his desire to spend a term abroad in Prague, Czech Republic as part of a cooperative program with Czech Technical University, which he did in the Fall of 2001.

In June of 2003 he earned his B.S. degree in Mechanical Engineering. Following his tenure at Union College he took a year off from school, working various jobs including stone masonry, mechanical equipment assembly, carpentry, and waiting tables at a brewery. After his short break from educational endeavors he chose to pursue a graduate degree at The Pennsylvania State University, where he planned on earning a M.S. and researching either combustion or fuel cell science.

In the summer of 2005 he began working for Professor Richard Yetter, and started examining several research projects including the study presented in this dissertation, as well as work in nanoscale metal particle combustion and propellant characterization. Through his positive experiences while working in the laboratory, his desire to continue learning at a high pace, as well as the urging of his advisor, colleagues, friends and family, he decided to pursue a doctoral degree. In May of 2007 he earned his M.S. for his studies involving the characterization of nanoaluminum, water and hydrogen peroxide solid propellants. Since that time he has continued to work the field of nanotechnology and its application in propellant and propulsion systems, as well as studying high temperature reactions related to combustion and propulsion systems. After the completion of his doctoral degree he plans to continue aerospace and defense related research in the private sector.