Failing Drop CO2 Deposition (Desublimation) Heat Exchanger for the Cryogenic Carbon Capture Process

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FALLING DROP CO\textsubscript{2} DEPOSITION (DESUBLIMATION) HEAT EXCHANGER FOR THE CRYOGENIC CARBON CAPTURE PROCESS

David W. James

A thesis submitted to the faculty of Brigham Young University in partial fulfillment of the requirements for the degree of Master of Science

Larry L. Baxter, Chair
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August 2011

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ABSTRACT

FALLING DROP CO₂ DEPOSITION (DESUBLIMATION) HEAT EXCHANGER FOR THE CRYOGENIC CARBON CAPTURE PROCESS

David W. James
Department of Chemical Engineering
Master of Science

Cryogenic carbon capture removes CO₂ and other pollutants from flue and waste stream gases produced from the combustion of fossil fuels such as coal, natural gas, and oil and the production of cement. A transient, 1-dimensional numerical model was developed to study the temperature profile within a counter-current surface CO₂ desublimation-falling liquid or solid heat exchanger. Effects of desublimation heat and mass transfer as well as convective and conductive heat transfer relationships were taken into account. Experiments show that CO₂ can be captured on a falling spherical particle when appropriate column operating conditions are met.

Keywords: heat exchanger, CO₂ desublimation, deposition, cryogenic carbon capture process
ACKNOWLEDGMENTS

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- The Department of Interior
- The Great State of Wyoming through the University of Wyoming
- Brigham Young University, College of Engineering and Technology, Department of Chemical Engineering
- Sustainable Energy Solutions LLC.

Although this research is in a different area of study than that originally commenced, appreciation is profoundly expressed to the professional influences outside of my chemical engineering department. Staff members at the National Energy Technology Laboratory in Albany Oregon demonstrated a love of research and understanding. I hope I will be able to find environments filled with such enthusiastic people wherever my career path ultimately leads.

I express appreciation for the attitude of my advisor, Dr. Larry L. Baxter. Even before he became my valued advisor he earned a great deal of respect and regards from me because of his inherent ability of teaching lessons that are applicable both in and out of the classroom. The guidance given as it relates to this work and other aspects of my university experience will have a lasting effect on my attitude towards others. He and the other faculty at Brigham Young University have provided an atmosphere that encourages learning and personal growth by maintaining an open, accessible, atmosphere of communication. It is a privilege to have attended
this university and to associate with the countless numbers of individuals who have helped
elevate my perspective to a new level.

Finally, special thanks are expressed to my wife for the love she provides for our two sons - Elias and Enoch - and me. I am grateful our Heavenly Father has allowed me to share the adventures of life with my family and I recognize His hand in all things. The epiphanies and other forms of inspiration provided during this undertaking have made the completion thereof possible.

David W. James
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## NOMENCLATURE

### Chemical Species

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>methane</td>
</tr>
<tr>
<td>CO</td>
<td>carbon monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>DEA</td>
<td>diethanolamine</td>
</tr>
<tr>
<td>DGA</td>
<td>diglycoamine</td>
</tr>
<tr>
<td>HFC’s</td>
<td>hydrofluorocarbons</td>
</tr>
<tr>
<td>Hg</td>
<td>mercury</td>
</tr>
<tr>
<td>MDEA</td>
<td>methyldiethanoloamine</td>
</tr>
<tr>
<td>MEA</td>
<td>monoethanolamine</td>
</tr>
<tr>
<td>N₂</td>
<td>nitrogen</td>
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<tr>
<td>NO</td>
<td>nitric oxide</td>
</tr>
<tr>
<td>NO₂</td>
<td>nitrogen dioxide</td>
</tr>
<tr>
<td>O₂</td>
<td>oxygen</td>
</tr>
<tr>
<td>PFC’s</td>
<td>perfluorocarbons</td>
</tr>
<tr>
<td>PVC</td>
<td>polyvinyl chloride</td>
</tr>
<tr>
<td>SF₆</td>
<td>sulfur hexafluoride</td>
</tr>
<tr>
<td>SO₂</td>
<td>sulfur dioxide</td>
</tr>
<tr>
<td>TEA</td>
<td>triethanoloamine</td>
</tr>
</tbody>
</table>

### Symbol and Meaning

- **A, B, C, D, and E** coefficients for various correlations
- **A** droplet surface area \( \text{L}^2 \)
- **a_p** acceleration of particle \( \text{L/t}^2 \)
- **C_D** drag coefficient
- **C_p** heat capacity \( \text{moleL}^2/\text{t}^2\text{T} \)
- **d_p** diameter of particle \( \text{L} \)
- **d_{po}** initial diameter of particle \( \text{L} \)
- **D_{αβ}** Binary diffusivity for the pair \( α-β \) \( \text{L}^2/\text{t} \) in a multi-component system
- **F_{i, db}** force component of drag or buoyancy \( \text{ML/t}^2 \)
- **g** gravitational acceleration \( \text{L/t}^2 \)
- **g, l, s** denotes physical state of gas liquid or solid -
- **G** H-TS = G Gibbs energy \( \text{moleL}^2/\text{t}^2\text{T} \)
- **H** U+PV = H Enthalpy \( \text{moleL}^2/\text{t}^2\text{T} \)
- **K** thermal conductivity \( \text{ML/t}^3\text{T} \)
- **k_{xm}** mass transfer coefficient \( \text{mole/tL}^2 \)
- **m_p** mass of the particle \( \text{M} \)
- **MW_i** molecular weight of species \( i \) \( \text{M/mole} \)
\( N \)  
number of particles

\( N_a \)  
mole transfer rate  
mole/s

\( n \)  
moles  
mole

\( P \)  
pressure  
M/Lt^2

\( P_c \)  
critical pressure  
M/Lt^2

\( R \)  
radius  
L

\( r \)  
radius  
L

\( R_f \)  
radius to the frozen solid zone  
L

\( R_g \)  
gas constant  
moleL^2/t^2T

\( S \)  
entropy  
moleL^2/Tt^2

\( t \)  
time  
t

\( T \)  
absolute temperature  
T

\( T_\infty \)  
bulk temperature  
T

\( T_c \)  
critical temperature  
T

\( T_0 \)  
initial temperature  
T

\( URF \)  
under relaxation factor

\( v_p, v_g \)  
velocity of particle, gas  
L/t

\( v \)  
terminal velocity of particle  
L/t

\( W_{ao} \)  
mole transfer rate  
mole/t

\( W_{po} \)  
initial weight of particle  
M

\( x_i, y_i \)  
mole fraction of species i  
-

**Dimensionless Numbers**

\( Nu \)  
Nusselt number

\( Pr \)  
Prandtl number

\( Re \)  
Reynolds number

\( Sc \)  
Schmidt number

\( Sh \)  
Sherwood number

**Greek Symbols**

\( \gamma \)  
surface tension  
M/t^2

\( \Delta \)  
change in some property  
-

\( \theta \)  
blowing factor

\( \kappa \)  
surface tension coefficient  
-

\( \kappa/\varepsilon \)  
Lennard-Jones parameter  
T

\( \mu_v \)  
viscosity of gas  
M/Lt

\( \pi \)  
3.14159…  
-

\( \rho, \rho_s, \rho_p, \rho_g \)  
density solid, liquid, particle, gas  
M/L^3

\( \sigma \)  
collision diameter  
L

\( \phi_{ab} \)  
collision integrals  
-

\( \Omega_{a,b}, \Omega_{a}, \Omega_{b} \)  
collision integrals  
-
1 Introduction

1.1 Background

On April 2, 2007, in Massachusetts v. EPA, 549 U.S. 497 (2007), the United States Supreme Court found greenhouse gases are air pollutants covered by the Clean Air Act. The following April 24th, the EPA Administrator signed a proposal under section 202 (a) of the Clean Air Act proposing to find that the current and projected concentrations of the mixture of six key greenhouse gases or gas categories – carbon dioxide (CO$_2$), methane (CH$_4$), nitrous oxide (N$_2$O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF$_6$) – in the atmosphere threaten the public health and welfare of current and future generations. This is referred to as the endangerment finding (US Environmental Protection Agency 2009).

Global CO$_2$ emissions have many sources. CO$_2$ can come from combustion processes within power generation, the residential and commercial building sectors, industrial processes such as cement, iron, and steel production, oil refining, hydrogen and ammonia production, natural gas purification, the transportation sector of the economy, and a plethora of other sources (Davison and Kelly 2005). Although an endangerment finding under one provision of the Clean Air Act would not by itself automatically trigger regulation under the entire Act, federal, academic, and industry energy sectors have continued collaborative efforts to find viable means of clean power generation technologies that will avoid economic losses that may result as
greenhouse gas taxation, prohibition, or regulations ensue. Evidence of this is increasingly seen in the development of consortium groups whose primary goals are “to advance the understanding of science, engineering policy and economics of CO₂ capture and geological storage (CO₂ Capture Project 2008).”

Some may envision a future of non-fossil fuel energy generation. However, technology and infrastructure are not in place to make this picturesque outlook the present reality (Baxter 2009). In 2009, the Department of Energy (DOE) indicated that fossil fuels supply 85% of the nation’s energy (US Department of Energy 2009). As all fossil fuel combustion processes yield CO₂, carbon separation and sequestration technologies are and have been developed to reduce CO₂ emissions into the atmosphere (Schianni 1976; Holmes and Ryan 1982; Herzog 1991; Brockmeier, Jody et al. 1994; Meisen 1997; Meratla 1997; Herzog 1999; Chou 2004; Aaron 2005; Clodic, El Hitti et al. 2005; Davison and Kelly 2005; Ali 2007; McGlashan 2008; Baxter, Baxter et al. 2009; Tuinier, van Sint Annaland et al. 2009).

As defined by the U.S. DOE Office of Fossil Energy National Energy Technology Laboratory (NETL), “geologic sequestration encompasses the processes of capturing and storing CO₂ that would otherwise reside in the atmosphere for long periods of time. … Geological sequestration involves the separation and capture of CO₂ at the point of emissions followed by storage in deep underground geologic formations (US Department of Energy 2008).” Practical geological storage sites exist near most industrial CO₂ sources. However, capture processes must precede the sequestration processes, the former involving far larger technical risk, energy consumption, and cost than the latter. Specifically, the leading technologies for CO₂ capture from coal-fired power plants include solvent absorption and oxy-fuel combustion. The former is
typically an amine-based scrubbing and desorption process while the latter involves separating oxygen from air and firing the system with a combination of purified oxygen and recycled flue gas. These technologies and their associated CO₂ storage processes would consume nearly 1/3 of the energy output from the power plant and could increase the cost of power production from such a plant by 80%. CO₂ transportation, storage, and monitoring represent about 10% of this cost, with storage itself representing only about 1% [DOE reports]. These statistics establish the clear need for better technologies, and the greatest room for improvement is in separation technologies.

Long before greenhouse gases were recognized as a potential threat to life, industry separated and captured CO₂ from other gases. CO₂ separation and formation minimization involve both post and pre-combustion methods. A method which utilizes the reversal of the reaction proposed by DuMotay and Marechal, in which lime was used to aid the gasification of carbon by steam, goes back as early as 1867 (Squires 1967). As discussed by Herzog, CO₂ separation and capture gained widespread attention as a possible economic source for its use in enhanced oil recovery operations in which CO₂ is injected into oil reservoirs to increase the mobility of the oil. Several CO₂ capture plants were constructed in the late 1970’s and early 1980’s within the U.S. and Canada in an effort to capitalize on this enhancement. These facilities utilize solvent extraction and extractive distillation techniques (Herzog, Drake et al. 1997; ZareNezhad 2009).

The monoethanolamine (MEA) solvent commonly extracts CO₂ from natural gas in a process called sweetening developed over 70 years ago. According to the Gas Processors Suppliers Association (GPSA), MEA solvent extraction is only one of the various CO₂ capture
and separation technologies that exist. Examples of post combustion CO₂ capture processes could include: (i) other solvent-extraction amines such as diethanolamine (DEA), diglycoamine (DGA), methylidiethanolamine (MDEA), and triethanolamine (TEA); (ii) membrane separation processes; (iii) molecular sieves; and (iv) cryogenic fractionation as well as (v) other procedures that are currently being developed (GPSA 1998; Herzog 1999; Davison and Kelly 2005; CO2 Capture Project 2008; McGlashan 2008).

Pre-combustion CO₂ separation techniques include oxyfuel-firing processes, which involve burning fossil fuels in pure oxygen rather than with air. This results in more complete combustion with an exhaust stream of nearly pure CO₂ and water vapor, simplifying the CO₂ separation and purification. Furthermore, the process can reduce NOₓ emissions. The primary challenge of this method stems from the initial separation of O₂ from air. O₂ separation from air is expensive and energy intensive relative to the overall process. Even though this process can generate nearly pure CO₂, it consumes comparable amounts of energy and has similar economic impact as the solvent-based systems.

Present operational methods of post-combustion and oxyfuel firing can only effectively capture around 90% of the CO₂ in flue gas and there is still is a large difference between captured and abated or avoided CO₂, with the former being far greater than the latter. Inevitably, greenhouse gases will be emitted into the atmosphere using industry’s current technologies. Any un-captured emissions will continue to contribute to unabated CO₂ in the atmosphere, which, implies that the greater capture efficiency, the better. Without carbon emission taxes, government subsidies or other requirements, society will continue to release CO₂ and other greenhouse gases into the atmosphere rather than capture and/or sequester them. It will always
be cheaper to release greenhouse gasses than capture and sequester them without an outside restriction put into place. However, with future taxation in mind as well as negative environmental and social consequences expected, researchers actively pursue other separation techniques, one of which provides the motivation for this work.

1.2 The Cryogenic Carbon Capture Process

The cryogenic carbon capture (CCC) process proposes a substantial decrease in both cost and energy consumption compared to solvent- and oxygen-based CO$_2$ capture systems. CCC is related to but not the same as cryogenic fractionation. It promises to reduce both energy and cost demands by more than a factor of 2 and maintains efficient operation at high (> 99%) capture efficiencies. Brigham Young University (BYU) and Sustainable Energy Solutions LLC (SES) cooperate in the development of this process. The following process description provides the context for the work described in this thesis.

The CCC process cools flue gas such that CO$_2$ desublimates. (Baxter 2008; Baxter 2008; Baxter 2008; Baxter 2009; Baxter, Baxter et al. 2009). There are several ways to accomplish this cooling, one of which – the compressed flue gas or CFG embodiment – appears in process flow diagram form as Figure 1-1. An alternative process, the external cooling loop (ECL) embodiment, does not involve flue gas compression or expansion but otherwise is similar to the CFG process.

The CCC process dries and cools flue gas from existing systems, modestly compresses it, using a recuperative heat exchanger - cools it, expands the gas through a turbine to further cool it, precipitates an amount of CO$_2$ as a solid that depends on the final temperature, pressurizes
and reheats the CO$_2$ and the remaining flue gas by cooling the incoming gases in a recuperative heat exchanger, and delivers an atmospheric pressure light gas for the stack and a pressurized CO$_2$ stream for storage. The final result is the CO$_2$ in a liquid phase and a gaseous nitrogen stream. (Figure 1-1). (Baxter 2009) After separation, the pressurized CO$_2$ liquid could eventually be sequestered or used in some other industrial/chemical process such as enhanced oil recovery.

Models of the CCC process indicate 20 – 80 % less energy consumption per unit of CO$_2$ avoided than solvent extraction or oxyfuel process (Baxter, Baxter et al. 2009). By improving the energy efficiency of the CCC process even further, the process can be greatly improved overall. The details of the heat exchanger represent one critical aspect of this process and the focus of this work. CO$_2$ desublimates in some sections of the heat exchanger, creating potential fouling or frosting problems. Furthermore, the process efficiency improves as temperature differences in
the heat exchangers are minimized. These heat exchanger design issues represent the central focus of this thesis.

1.3 Motivation for this Thesis

As currently available commercial heat exchanger modeling software does not provide an adequate means of predicting desublimation-phase-change of stream components, the present investigation was undertaken. This investigation models a proposed cryogenic CO$_2$ capture process heat exchanger system that consists of vertical countercurrent heat exchangers in which waste flue gas is cooled to approximately 135 K by condensed phase spheres entrained in the flue gas and reports initial results from a prototype of such a heat exchanger.

The model developed during this investigation incorporates various heat and mass transfer relationships. This document explains how the model quantifies CO$_2$ desublimation and describes temperature and composition profiles of the particle and the bulk gas streams. This model reveals some of the important mechanisms of CO$_2$ desublimation on a falling spherical particle.

1.4 General Statement of the Problem

Efforts to improve and optimize the CCC process efficiency rely on models that include detailed thermodynamic, heat transfer, and mass transfer relationships that are beyond the scope of even the most sophisticated process modeling programs currently available. Analytical solutions are limited due to the mathematical complexity of the process. To be applicable, a model must provide heat exchanger design (size and flow rate) information for conditions that
include desublimation of gases to their respective solid phase. Properties vary as a function of time, space, and have inherent temperature dependencies.

Heat, mass, and momentum transfer issues and heat exchanger efficiency improvements as they relate to the treatment of flue gas represent the heart of this project. The heat exchanger model is based on a vertically falling drop flowing counter-currently with the gas in heat exchangers in which a CO2-rich waste gas stream is cooled from 175 K (near the frost point of CO2 in typical flue gases from coal-fired power plants) to approximately 135 K. Model pressures can range from ambient to several bar. This model simultaneously solves the momentum, energy, species continuity, and overall continuity equations for the solid and gas phases in a steady-state one-dimensional heat exchanger.

1.5 Counter-Current-Heat Exchanger

For a counter-current, falling-particle heat-exchanger design, an exchange medium is introduced at the top of the column and flue gas is introduced at the base of the column. Temperature and pressure conditions permit surface desublimation wherein components of flue gas, such as CO2 and SO2, can nucleate around the falling particle exchange medium. Desublimation occurs as long as the Gibbs energy of the solid CO2 at the surface temperature is less than that of the vapor, or, equivalently, as long as the CO2 vapor pressure at the temperature of the condensed phase exceeds the CO2 partial pressure in the gas. The exchange medium and desublimated CO2 solids separate in a loop outside the heat exchanger column that is not discussed in this work.
The solids will be pressurized before further treatment and eventual sequestration. Exit flue gas may undergo additional treatment down-stream in the cryogenic carbon capture process before being vented into the atmosphere, although the CCC process removes most of the other pollutants in the gas more effectively than current technologies. Figure 1-2 is a simplified flow diagram representative of the heat exchanger.

Environmentally significant trace gas species in flue gases include NO, NO\textsubscript{2}, SO\textsubscript{2}, SO\textsubscript{3}, Hg, HCl, and potentially other compounds. In addition, there are significant oxygen (several percent) and moisture components in the gas. This investigation focuses on CO\textsubscript{2} removal, so the simulated flue gas includes only N\textsubscript{2} and CO\textsubscript{2}. In addition, the exchange medium may form vapors, which are also treated in this work. Table 1 lists the physical states of the species accounted for within the model.
### Table 1 Flue gas components and physical states accounted for within the desublimating heat exchanger model

<table>
<thead>
<tr>
<th>Component</th>
<th>Physical State</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>g, s</td>
</tr>
<tr>
<td>N$_2$</td>
<td>g, l or g, s</td>
</tr>
<tr>
<td>Exchange media</td>
<td>g, l or g, s</td>
</tr>
</tbody>
</table>

Although water is a primary combustion product and is included in flue gas, it was not incorporated within the model since it is removed prior to this process step by other mechanisms. Hg is also not included within the model as it is generally present in flue gas streams in trace amounts (ppb) and it has no measurable effect on heat or mass transfer. Research colleagues have experimentally and theoretically investigated and reported the fate of the environmentally sensitive flue gas components (Baxter, Baxter et al. 2009; Bence, James et al. 2010; Burt, Baxter et al. 2010; Larsen, Fox et al. 2010). Oxygen, like nitrogen, is chemically inert in this process.

### 1.6 Scope of the Thesis

The current investigation focuses on thermodynamic and transport properties of the heat exchanger including the velocity, composition, and temperature profiles of the heat exchanger. The model uses a 1-dimensional design to describe heat exchanger conditions and solves the transient heat and mass transfer rates for both the condensed and gas phases, both treated in a Lagrangian framework. Microsoft Excel is the user interface and computational engine. As shown later, the model predicts that temperature profiles are highly dependent on initial particle size, exchange media and flue gas flow rates, as well as flue gas initial composition. Furthermore, the model describes desublimation of CO$_2$ at heat-exchanger-pressure conditions near 1.0 bar and heat-exchanger-temperature conditions between ~135 K and 175 K.
2 Literature Review

This literature review includes four sections. Section 1 describes current industrial dry ice production techniques. Section 2 is a discussion of surface desublimation as it relates to CO$_2$. Section 3 details possible heat exchanger types that could be used to accomplish the goals of the CCC process. Finally, Section 4 depicts some of the pitfalls with CO$_2$ desublimation predictions as well as properties of the components of the flue gas and exchange fluids.

2.1 Industrial Solid CO$_2$ Production Techniques

Although solid CO$_2$ is used in many processes that take advantage of the phase changes of the compound, commercial dry ice is not generally produced through desublimation. In commercial applications, CO$_2$-rich gas is pressurized and refrigerated until it condenses into its liquid form. When pressure is quickly reduced by exposure to warmer temperature some of the liquid CO$_2$ will vaporize. The vaporization causes a rapid lowering of the temperature of the remaining liquid CO$_2$. As a result, the liquid freezes. The snow-like solid CO$_2$ produced is then compressed with hydraulic pressure into either small pellets or larger blocks of dry ice.

Obviously, this method of capturing CO$_2$ will not work for industrial processes trying to remove greenhouse gases from waste streams, as the purpose of carbon dioxide capture
processes is to efficiently produce a liquid CO$_2$ slurry stream that can be pumped and sequestered into underground saline aquifers.

Baxter et al. relate (Baxter 2009) that CO$_2$ capture efficiency depends primarily on the pressure and temperature at the end of the expansion process. At ~1 bar, the CCC process captures 99% of the CO$_2$ at 138.15 K (-135°C, -211°F) and 90% of the CO$_2$ at 153.15 K (-120°C, -184°F). By operating at these conditions energy can be saved. As thermodynamics and equipment considerations play a vital part in ensuring heat exchanger conditions are met it is important to understand their role in a process undergoing desublimation phase changes.

### 2.2 CO$_2$ Surface Desublimation

Although the majority of previous work describing desublimating processes is not related to CO$_2$ separation, the primary concepts described are still applicable to heat exchanger modeling. Geometry, operating conditions, and heat transfer within a process undergoing desublimation are relevant. For example, even though phthalic and maleic anhydride or benzoic acid are not found in flue gas mixtures, the equations that describe desublimation have been studied for these species in cylindrical and fin shaped coordinates for some time (Gorelik, Amitin et al. 1980; Hastaoglu and Baah 1991). Similar to the expansion section of the CCC process is the work of Kodde which describes desublimation of aerosol mixtures by sudden expansion (Kodde and Mewes 1995; Wagner and Mewes 2000). Desublimation of sulfur containing species because of a sudden expansion is also addressed in the design of natural gas pipeline processes where this can frequently occur (Pack 2005; Cezac, Serin et al. 2008).
Closer related to a CO₂ desublimation heat exchanger is found in the work of Shchelkunov and Rudenko et al. which describes surface desublimation experiments of CO₂ in binary gas mixtures. However, their experiments were undertaken at high pressure and on a flat plate (Shchelkunov, Rudenko et al. 1986). Their work does indicate that, despite having an isothermal plate, the concentration of the CO₂ in the gas stream is highly related to precipitate growth. Both Hastaoglu, and Gevorkyan et al. found a similar relationship of desublimation rates for phthalic anhydride based on the composition of the contact gases (Gevorkyan, Ermakova et al. 1980; Hastaoglu and Baah 1991).

The study of desublimation phase changes on spherical objects has also been addressed. As cited in Hastaoglu (Hastaoglu and Baah 1991), desublimation on spherical objects is addressed in the work of Korobchanskii et al. (Korobchanskii, Grebenyuk et al. 1981) and Gelperin et al. (Gel'perin, Lapshenkov et al. 1979). Though the details of experimentation are limited, Korobchanskii et al. developed a process where target components were desublimated on falling metal spheres that came in contact with rising vapor-gas mixtures. Gelperin et al. described the desublimation of naphthalene on small spherical seed particles within a fluidized bed (Gel'perin, Lapshenkov et al. 1979). Although neither of these projects were intended to describe a heat exchanger, but a means of separating a component from a gas stream, it is significant in that the operation of fluidized beds and spray towers can be modeled with geometry related to sphere particles.

Spherical geometry is especially relevant in the work of Ford and Lekic. They studied the rate of growth of droplets during condensation (Lekic 1970; Ford and Lekic 1973; Lekic 1976; Lekic and Ford 1980) for use in heat exchanger spray towers. Many of the ordinary differential
equations used to solve temperature profiles for condensation growth are similar to the equations which describe desublimation growth rates. However, many of the simplifications used in previous works, although related, were not applicable at the temperatures and reactor conditions anticipated within a cryogenic desublimation heat exchanger.

2.3 Heat Exchanger Designs

Three heat exchanger designs were originally discussed for application within the CCC process. These include fluidized bed, bubble column, and falling sphere heat exchangers. Each design is briefly discussed in the following sub-sections.

2.3.1.1 Fluidized Bed

Heat exchangers come in a variety of forms. A fluidized bed is one possible heat exchanger for the CCC process. Within a CO$_2$-desublimating fluidized bed would be found vertical heat exchanger coils. However, this arrangement is in contrast to that found in most fluidized beds in that the coils would extend from the base rather than the top of the heat exchanger (Cole and Allen 1979; Gel'perin, Lapshenkov et al. 1979; Tabatabaie-Farashahi, Upadhyay et al. 1981; Davis 1982; Ahn, Bae et al. 2005; Stefanova, Bi et al. 2008). A diagram of this process is included in Figure 2-1.

The downside of this coil arrangement includes the potential CO$_2$ buildup on the coils. However, Cole et al. showed the benefit of scale removal in a fluidized bed containing sand and geothermal water. It is theorized that solid CO$_2$ particles bombarded with CO$_2$ on the surface of a coil could provide a similar cleaning effect. Even though cryogenic liquid CO$_2$ can be used as a
cutting tool for stainless steel (Gibbs, Pendlebury et al. 1974; Holmes, Hill et al. 1974; Surman, Brown et al. 1974; De Chiffre 2007) as presented by Larsen et al., stainless steel has a Mohs hardness greater than solid CO$_2$ and is unlikely to cause erosion of the coils or turbines at the conditions of the CCC process. In Larsen’s work, surface cleaning was witnessed but gross erosion was not observed. Figure 2-2 shows surface cleaning of 304 stainless steel (Larsen, Bean et al. 2010).

Unhampered by potential erosion of stainless steel by solid CO$_2$, an arrangement in which the solid CO$_2$ particles were fluidized within the coil region could theoretically remove the desublimated solids on the coils as well as have desublimation occur on the seed particles
themselves. The benefits of this proposed heat exchanger are still being considered and are the subject of another research project outside the bounds of this thesis. Many of the relationships and the accompanying descriptive equations fundamental to modeling a fluidized bed are found in the book by Gibilaro (Gibilaro 2001).

## 2.3.1.2 Bubbling Heat Exchanger

In a countercurrent-bubbling heat exchanger, small bubbles of warm CO$_2$ rich gas are passed through a cold exchange fluid medium in which heat transfer occurs. CO$_2$ should desublimate at the gas-liquid interface. The exchange fluid must have a density lower than the solid CO$_2$ at operating temperatures for this method to work. Based on specific gravity difference, solids will travel with the liquid and gas will rise to the top of the heat exchanger for further processing. The solids and the liquids will be separated and the exchange fluid recycled through the system. This process design provides the benefit of a larger interfacial area for contact of the gases and exchange fluid. Drawbacks to this design include the amount of exchange fluid that would be needed to process the tons per day order of magnitude of CO$_2$ present in a flue gas stream and the energy efficiency loss of separating any adsorbed CO$_2$ within
the exchange fluid. Furthermore, this design has the potential for clogging due to freezing within a column if chevron separators at various stages are used. A simplified diagram of this proposed heat exchanger is found in Figure 2-3.

![Diagram of the CO₂ Desublimation Bubble Heat Exchanger](image)

**Figure 2-3 Diagram of the CO₂ Desublimation Bubble Heat Exchanger**

### 2.3.1.3 Falling Sphere Heat Exchanger – Drops and Solids

A falling sphere heat exchanger, as previously described using Figure 1-2, is similar to atmospheric and mechanical spray towers discussed by the Gas Processors Suppliers Association, among others (Korobchanskii, Grebenyuk et al. 1981; GPSA 1998; Lenntech 1998-2009; Canara Engineers Pvt. Ltd. 2010). These types of heat exchangers are generally used when low performance can be tolerated and when small sizes are required. This heat exchanger has the benefit of lower operational costs than other types of heat exchangers. It is anticipated
that similar design considerations, such as horizontal or vertical flow cross flow pattern orientations should be adhered to. Processes that anticipate potential freezing recommend a vertical orientation (Hollands 1974; Katta and Gauvin 1975; Gauvin and Katta 1976; Canara Engineers Pvt. Ltd. 2010).

Although spray tower heat exchangers have similar design aspects, these heat exchangers are not the same as a CO\textsubscript{2} surface desublimation heat exchanger. These heat exchangers work off of the premise of a colder falling droplet travelling counter currently through a warmer gas media. In the case of spray towers, the droplets generally undergo evaporation and the liquid nucleation site is cooled with the loss of vapor. Whereas for a falling droplet heat exchanger, the solids undergo desublimation and the exchange liquid absorbs the heat released during this process and hence warms. Similarly, if solid spheres were used as the exchange medium, they would absorb the heat released. Like unto the bubble column discussed previously, this design also requires a considerable amount of exchange media to process the tons per day order of magnitude of CO\textsubscript{2} present in a flue gas stream and will have the energy efficiency loss of separating solid CO\textsubscript{2} from the exchange media. However, unlike the countercurrent bubble column, this heat exchanger will be less prone to issues that may arise from clogging within the heat exchanger. If solid spheres are used as an exchange media, the handling and cooling of the spheres may be more energy intensive than other heat exchanger designs.

### 2.4 On Phase Changes

Phase equilibrium plays a vital role in heat exchanger design. The highest recovery of CO\textsubscript{2} and other pollutants will be the equilibrium value. Phase equilibrium recovery values may be different than steady state conditions and does not account for mass transfer to a heat transfer
surface. There exist two primary ways in which solid CO$_2$ may be formed within any exchange fluid-based heat exchanger design. If CO$_2$ is adsorbed to such a limit that it exceeds its solubility limit within the solution, it will crystallize or precipitate out. Likewise, if the CO$_2$ content of the vapor exceeds the solubility limit, CO$_2$ will desublimate.

Eggeman discusses some of the methods of predicting frost points as they relate to the two methods of CO$_2$ solids production within a process (Eggeman 2005). However, Eggeman’s work was intended to aid in frost point calculations and was not intended to describe the rate in which CO$_2$ will desublimate within a process. Figure 2-4 shows the highest amount of normalized recoverable CO$_2$ and SO$_2$ at 1.1 bar with the initial mole fractions shown on the graph. This calculation is based on solid vapor pressure calculations and not upon transport properties, which are more limiting.

Based on the plots shown, a gas temperature of ~137.8 K at the surface of the particle would capture 99% of the CO$_2$ at 1.1 bar. At temperatures greater than 173.6 K CO$_2$ will not desublimate at the conditions given.

2.5 Fluid Properties and Pitfalls of CO$_2$ Desublimation Predictions

To model the countercurrent falling sphere heat exchanger, several properties of the exchange fluid and flue gas mixture must be known over the series of temperatures and pressures that will be present in an apparatus. The empirical relationships describing gas mixture viscosity, thermal conductivity, and diffusivity, among other properties, are not trivial in nature. These properties must be taken into account to provide sizing estimates for the heat exchanger’s implementation in pilot and full-scale operations. Descriptions of many of the transport
Figure 2-4 Normalized Recovery Fraction of Solid CO\textsubscript{2} and SO\textsubscript{2} as well as Liquid SO\textsubscript{2} based on the initial mole fractions shown and an operating pressure of 1.1 bar as a function of surface temperature.

relationships needed are found in the compilation of transport equations provided in *Transport Phenomena* by Bird, Stewart, and Lightfoot (Bird, Stewart et al. 2002). Physical properties of the various species were found using the DIPPR database through *Diadem Pro* as well as an in-house database - consisting of the reported results of thermodynamic properties - maintained by our research group at Brigham Young University (Rowley, Wilding et al. 2006).

2.5.1 Exchange Fluid Media Data Available

Several exchange fluids have been found to be potentially useful for all the proposed heat exchangers. To be useful, the exchange fluid must not freeze at heat exchanger operating conditions, should have a low vapor pressure, should have a viscosity that permits the fluid to be
readily pumped without a great deal of increased capital and operational cost, and should be environmentally less toxic. Using the DIPPR database (Rowley, Wilding et al. 2006) a series of compounds has been found to be potentially useful. The liquid phase compound that can easily be included within the model is found in Table 2. Due to the pungent odor of this compound, it is unlikely to be used in full-scale processes, but does show the model’s capacity for use in heat exchanger sizing.

**Table 2 Properties of the compound included as the exchange fluid within Surface-CO$_2$ Desublimation Falling-Drop Heat Exchanger model**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Freezing Point, K</th>
<th>Vapor Pressure, Pa @ 130 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutyl Mercaptan</td>
<td>128.31</td>
<td>8.017E-06</td>
</tr>
</tbody>
</table>

Although some compounds, such as ethane, have a higher vapor pressure than desired, they may still be useful if they were used in a blend. Blending refrigerants is often seen within cryogenic processes, such as liquid natural gas processes, and is recommended by Holmes and Ryan (Holmes and Ryan 1982; Holmes and Ryan 1982; Herzog 1999). The benefits of blended proposed heat exchanger refrigerant liquid are being considered and are the subject of another research project outside the bounds of this thesis.
3 Droplet Model Description and Development

Modeling desublimation processes involves simultaneous heat and mass transfer and, in this case, momentum transfer while tracking phase changes. Existing process simulation packages accurately describe condensing heat exchangers that do not involve counter-flowing phases, but they are not capable of dealing with solids generally or, in the most sophisticated of them, solids that form or are destroyed in heat exchangers, expanders, and other non-reactor unit operations. In this investigation, a one-dimensional model for spherical shapes describes heat and mass transfer rates, momentum exchange, and thermodynamics in both phases. The model predicts transient temperature, velocity, pressure, composition, mass and heat transfer rates, and related data as a function of time/position within the proposed heat exchanger. This model can be easily modified to account for either solid or liquid exchange mediums.

The objectives of this thesis are to model phase changes, such as desublimation and condensation, of components commonly found in waste flue gas streams that can occur in a countercurrent falling sphere heat exchanger. Microsoft Excel provides a convenient user interface and computational engine, supplemented by relaxation and other techniques to help with convergence.
3.1 Assumptions/Limitations

The following assumptions allow tractable mathematical model development:

- all properties are assumed to be transient and one dimensional in space;
- local thermal equilibrium exists between the solid and gas phase in the particle interface;
- the heat exchange medium is isothermal (for a solid sphere, the Biot number was compared to ensure this assumption is valid);
- gas and particle velocity are uniform in the column (one dimensional analysis with changes only in the axial dimension);
- particles are distributed uniformly throughout and are equally displaced;
- particles do not coalesce or atomize as they fall through the column; and
- surface desublimation on the walls of the column is not included.

3.2 Boundary Conditions

The model is comprised of 128 zones spaced throughout a vertical column. Numbering for the nodes begins at the top of the column or the 0 position. Length within the column is quantified such that negative is progression in the downward direction and positive the upward direction. Simulated flue gas is introduced at the bottom of the column and leaner gas exits through the top of the heat exchanger. Likewise cold particles are introduced countercurrently to the gas at the top of the column such that desublimated, solid CO$_2$ exits with the solids or liquid exchange medium through the bottom of the column. A basic diagram representing this setup is found in Figure 3-1.

Although the model uses a one-dimensional approach (Figure 3-2), gas flow around a sphere is at least two-dimensional. Figure 3-3 depicts a two-dimensional steady-state velocity
Figure 3-1 Basic diagram representing column boundary conditions

profile. As indicated by Roberts in an unrelated experimental and modeling procedure for spherical particle combustion, a more realistic approach would include a stagnation point on the upwind side of the sphere. The sides of the sphere would include a more fully developed boundary layer, and on the downwind side of the sphere, a recirculation zone would develop (Roberts 2006).

The flow pattern indicates that non-uniform heat and mass transfer around the sphere is more likely. However, with a one-dimensional model (assuming the flow is axial-symmetric
around the particle), the film layer could be described by simply setting the boundary conditions at an arbitrarily long distance from the particle and solving the transport equations (Roberts 2006).

**Figure 3-2** Diagram depicting path of temperature profile calculations

**Figure 3-3** Representative velocity contours - falling particle in a countercurrent fluid - colored by relative magnitude as compiled using ANSYSFLUENT 6.3, gas flows from bottom to top
3.3 Heat and Mass Transfer Relationships

The mean Nusselt number is useful for predicting forced convection heat and mass transfer to or from droplets or bubbles and assumes a constant surface temperature and composition. Although the particle will have an exterior shell of CO$_2$ steadily deposited on the surface of the solid exchange medium and possibly CO$_2$ desublimation in the boundary layer, this relationship provides an estimate useful for calculations. The Nusselt number depends on flow conditions as indicated in the following empiricism (Bird, Stewart et al. 2002)

\[
Nu \equiv \frac{h_k}{d_p} = 2.0 + 0.60Re^{1/2}Pr^{1/3}.
\]

(3-1)

Analogously for mass transfer, the Sherwood number is determined by the following relationship (Bird, Stewart et al. 2002)

\[
Sh \equiv \frac{k_mD_{AB}}{d_p} = 2.0 + 0.60Re^{1/2}Sc^{1/3}.
\]

(3-2)

The Nu and Sh correlations, shown above, describe the average heat and mass transfer in a non-reacting boundary layer well. For a one-dimensional model in spherical coordinates, the radial direction, $r$, cannot capture the effect of bulk flue gas flow around the particle except by changing the film thickness, which is the distance from the particle surface to the bulk conditions (Bird, Stewart et al. 2002; Roberts 2006). A one-dimensional model can only accurately predict the boundary layer characteristics when the bulk gas is stagnant when the bulk conditions include a thick film. By placing the bulk conditions closer to the particle, the heat and the mass transfer
rates accurately describe overall particle conditions even if axial flow is ignored and variations in the second dimension are ignored (Roberts 2006).

### 3.4 Particle Velocity Model

Two forces primarily act upon the particle. These include buoyancy and drag forces. The buoyancy force on a particle is given by

\[ F_b = \rho_g - \rho_p \frac{\pi d_p^2 g}{6}, \]

(3-3)

where \( g \) is assumed to be a negative number when it points down and the other symbols are standard, as defined in the Nomenclature Table (pages xxii-Error! Bookmark not defined.).

Drag force is taken from the definition of the coefficient of drag \( C_D \):

\[ C_D \equiv \frac{F_d}{\frac{1}{2} \rho_g v_{relative}^2 A_p} = \frac{8F_d}{\rho_g v_{relative}^2 \pi d_p^2}. \]

(3-4)

Upon rearrangement, this yields

\[ F_d = \frac{C_D}{8} \rho_g v_{relative}^2 \pi d_p^2. \]

(3-5)

where the direction of the force is in the opposite direction as the velocity difference. The following empiricism, for the drag coefficient, is assumed valid for \( Re < 6000 \) (Bird, Stewart et al. 2002). At \( Re > 6000 \), \( C_D \) is assumed to be simply 0.44.

\[ C_D = f = \frac{24}{Re} + 0.5407 = \frac{24 \mu_g}{v_g - v_p \rho_g d_p} + 0.5407. \]

(3-6)
The overall force balance equates these two forces with the particle acceleration

\[ m_p a_p = m_p \frac{dv_p}{dt} = F_i = \rho_g - \rho_p \frac{\pi d_p^3 g}{6} + \frac{C_D}{8} \rho_g v_{relative}^2 \pi d_p^2. \]

(3-7)

Normalized by mass this becomes:

\[ a_p = \frac{dv_p}{dt} = \frac{F_i}{m_p}. \]

(3-8)

Rearranged this becomes:

\[ v_{p,i} = \frac{F_i}{m_p} dt + v_{p,i-1}. \]

(3-9)

However, the velocity of the particle cannot exceed the terminal velocity; therefore, an iterative approach was used. Terminal velocity, \( v_{p,\infty} \), is the velocity at which the particle neither accelerates or decelerates, which a particle asymptotically approaches. It is given by rearrangement of the following:

\[ F_i = 0 = \rho_g - \rho_p \frac{\pi d_p^3 g}{6} + \frac{C_D}{8} \rho_g v_{relative}^2 \pi d_p^2. \]

(3-10)

Further rearrangement yields

\[ \frac{\rho_p - \rho_g}{\rho_g} \frac{4 d_p g}{3} = \frac{24 \mu_g}{v_{relative}^2 \rho_g d_p} + 0.5407 \frac{v_{relative}^2}{v_{relative}^2} \]

(3-11)
which has four roots, two real and two imaginary. The real root of importance is found in the following relationship:

\[ v_{p,\text{term}} + v_g = v_{\text{relative}} = -\frac{B - B^2 + 2B + 0.5407^2 + 4A}{2 \times 0.5407^2}, \]

(3-12)

where A is

\[ A = \frac{\rho_p - \rho_g}{\rho_g} \frac{4d_p g}{3}, \]

(3-13)

and B is

\[ B = \frac{24\mu}{d_p \rho_g}. \]

(3-14)

As long as the bulk flue gas velocity is less than the absolute value of the terminal velocity the particle will continue to fall.

The velocity of the particle determines the time the particle spends within a zone. Assuming a constant acceleration within a zone, the time of the particle in a zone is:

\[ t_p = \frac{2}{v_{p_l} + v_{p_{l-1}}}. \]

(3-15)
3.5 Mass Balance

The reaction rates, or rates of evaporation and desublimation, are found using the methods described by Bird, Stewart, and Lightfoot (Bird, Stewart et al. 2002), in which the molar desublimation and evaporation rates in one computational zone are similarly found using the following relationship.

\[ W_{ao,i} = \frac{k_{xm} \theta_{m,A} \pi d_{p,i}^2 N p_{vap}}{p_{total} x_{A,oo} + p_{vap}} \frac{p_{vap}}{p_{total}} W_{bi} \ . \]

In this equation, the mass transfer coefficients, \( k_{xm} \), come from the Sherwood number correlations shown earlier and \( j \) is the number of particles within a zone.

3.5.1 Mole Balance Gas Phase

The equations that predict the moles desublimated and evaporated in a computational cell form sink and source terms, respectively, for the gas-phase species balance. Desublimation reactions are not allowed to reduce the moles to less than zero. The CO\(_2\) and exchange fluid molar flow rates in the gas phase are:

\[ n_i = n_{i+1} + W_{ao,i+1} t \ . \]

(N3-17)

Nitrogen is not considered condensable at the conditions given in the reactor, so it is kept constant throughout.
3.5.1 Mole Balance Condensed Phase

Similarly for the condensed phase the mole balance for the CO₂ and exchange fluid species is given by:

\[ n_i = n_{i-1} - W_{ao}t . \]

(3-18)

This conserves the total moles.

3.6 Energy Balance

A series of relationships describe the heat supplied to the particle. Heat is transferred by convection, by that absorbed or lost from desublimation, sublimation, condensation and evaporation of species, and by conduction. Each path is interrelated with the others must be used appropriately to ensure that an energy balance is maintained.

3.6.1 Convection

The following relationship, which describes heat transfer by convection, is used:

\[ q = ANh_m \theta \ T_s - T_g . \]

(3-19)

3.6.2 Enthalpy

Heat transfer from convection is related to the condensed-phase total enthalpy changes with time according to the equation:
\[ \frac{dH_c}{dt} = q + A_i N_i \Delta H_{rxn,i}. \] (3-20)

where subscript \( i \) represents chemical species. Assuming that all terms are approximately constant across a computational cell, designated with superscript \( j \), the enthalpy balance can be written

\[ H_{c}^{j+1} - H_{c}^{j} \equiv \Delta H_{c}^{j} = \Delta t^{j} q^{j} + i N_{i}^{j} A_{i}^{j} \Delta H_{rxn,i}^{j}. \] (3-21)

where all droplets are assumed to have the same surface area and mass transfer rate, i.e., the droplet population is monodisperse.

The enthalpy change for the gas phase across a zone must be equal but opposite in magnitude to the condensed phase heat transfer rate \( q \) across same zone. The particle or droplet enthalpy is calculated by:

\[ H_{c}^{j+1} = H_{c}^{j} + \Delta H_{c}^{j}. \] (3-22)

Solid CO\(_2\) enthalpy is based on a heat capacity relationship modified from that found in the DIPPR database. This modified version accounts for the heat of formation for the species and has the form:

\[ H_{CO_{2,s}} = A_{CO_{2}} T + \frac{B_{CO_{2}} T^{2}}{2} + \frac{C_{CO_{2}} T^{3}}{3} + \frac{D_{CO_{2}} T^{4}}{4} + \frac{E_{CO_{2}} T^{5}}{5} + F_{CO_{2}}. \] (3-23)

Other coefficients needed to determine the enthalpies of the various species come from a
database for many species maintained by our research group and derived from many literature sources. The form of the equation that describes species enthalpies in this database is:

\[ H_i = -\frac{A}{T^2} + B + \frac{CT}{2} + DT^2 + \frac{E}{T} \cdot R_g T. \]

(3-24)

3.6.3 Particle Temperature Profile

A spherical droplet with no internal circulation or volume change transfers heat in three distinct regions. These include: the liquid region composed of the exchanger fluid, the solid region composed of the desublimated CO₂, and the gaseous region composed of CO₂, N₂, and vaporized exchanger fluid (Figure 3-4). However, because the ratio of exchange fluid medium to solid build up is large and internal circulation is likely, for the purpose of this model, the temperature of the particle is considered the same as the surface of the particle. A uniform temperature throughout the particle is only valid for a Biot number much less than 1.

![Figure 3-4 Theoretical Temperature Profile of a Spherical Droplet Encased in a Solid Shell](image)
To determine the bulk temperature of the gas phase and surface temperature of the particles, the relationship between enthalpy and temperature is used. Within the relationship described in Equations (3-23 and (3-24), the B coefficient usually dominates the temperature dependence of the calculated enthalpy. It is the only non-zero coefficient if heat capacity is constant. Therefore, rearrangement of this equation can provide the temperature of the gas phase by the following iterative relationship, which should converge rapidly if the B coefficient dominates. Similarly, for the condensed phase, the coefficients A and B for the exchange fluid dominate the temperature dependence of enthalpy. The following relationship is used to determine the temperature of the particle.

\[
T_{gas} = \frac{H_{gas} - I - \frac{A_I C_I T}{T} + D_I T^2 + \frac{E_I}{T} R_g T}{I B_I R_g}
\]

(3-25)

These iterative solutions converge rapidly to the correct temperatures.

3.6.1 Relaxation Method

For the model to work using Microsoft Excel, the iterative calculation must be enabled. Iterative calculations have inherent instability for a countercurrent process in that Excel generally performs calculations left to right and then top to bottom. An initial guess is always needed. Because the instability occurs within the model, an under relaxation factor (URF) is utilized. The
relaxation factor takes the values from the previous iteration to dampen the solution and cut out steep oscillations that may become present.

Calculations are continued until $T_{\text{calc}}$ and $T_{\text{new}}$ are virtually the same. As URFs approach a value of 0, the iterations become completely stable, but the converge rate stops. For this model, an URF of 0.1 is used. Relaxation techniques are required for bulk and particle temperature profiles, which are calculated using the following relationship:

$$T_{\text{new}} = URF \times T_{\text{previous}} + 1 - URF \times T_{\text{estimated}}$$

(3-27)

where $T_{\text{estimated}}$ is found using Equations (3-25 and (3-26).
4 Experimental Approach

A bench-scale experimental apparatus described below simulates this type of heat exchanger and provides data for model validation. However, due to safety protocols implemented by the university, this apparatus uses a solid sphere and not a flowing liquid. Most of the compounds identified as plausible candidates for experimentation are regulated by Brigham Young University for use within a Class I electrical safety areas, none of which exist or can reasonably be built within our research group.

The nature of the model makes it relatively easy to be modified for different species as long as the properties are known. Experiments were performed using a falling metal sphere surface desublimating heat exchanger designed and built as part of this project. A simplified process flow diagram of this project appears in Figure 4-1.

![Figure 4-1 CO₂ Desublimating on a Falling Sphere Heat Exchanger](image-url)
The experimental setup consists of four main sections including: (i) the cooling tower experimental apparatus, (ii) computer interface, (iii) the gas pre-cooler, and (iv) the exchange media cooler. Each section is explained in detail. Figure 4-2 depicts the parts of the experimental apparatus.
4.1 Cooling Tower

The main section of the experimental apparatus and design is found within the cooling tower. The tower includes 1.27 cm inner diameter copper tubing surrounded by Cryo-Lite fiberglass insulation and 7.62 cm diameter pvc casing. Cryo-Lite is produced by Lydall and is a fiberglass blanket made of high quality fine fibers bonded with a melamine resin (Lydall Industrial Solutions 2004). Each sheet is 1.905 cm thick.

All thermocouples of the experimental apparatus are Type K, twisted and shielded 24 AWG wiring with Neoflon PFA insulation. Thermocouple locations of the column appear in Table 3. Each thermocouple accesses the column through a 0.254 cm diameter inlet hole. Thermocouple placement was designed with statistical considerations and model validation in mind; for this reason, more thermocouples appear near the top and bottom of the column rather than being equally spaced.

Table 3 Thermocouple location for the Cooling-Spray-Tower Section of the Experimental Apparatus

<table>
<thead>
<tr>
<th>Thermocouple Identification</th>
<th>Relative Length from Top of Column (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>Within Exchange Reservoir</td>
</tr>
<tr>
<td>T2</td>
<td>Within Exchange inlet line</td>
</tr>
<tr>
<td>T3</td>
<td>2.06</td>
</tr>
<tr>
<td>T4</td>
<td>9.99</td>
</tr>
<tr>
<td>T5</td>
<td>12.22</td>
</tr>
<tr>
<td>T6</td>
<td>31.43</td>
</tr>
<tr>
<td>T7</td>
<td>50.01</td>
</tr>
<tr>
<td>T8</td>
<td>66.04</td>
</tr>
<tr>
<td>T9</td>
<td>97.79</td>
</tr>
<tr>
<td>T10</td>
<td>113.82</td>
</tr>
<tr>
<td>T11</td>
<td>118.75</td>
</tr>
<tr>
<td>T12</td>
<td>123.83</td>
</tr>
<tr>
<td>T13</td>
<td>130.81 Within Gas Inlet line</td>
</tr>
</tbody>
</table>

Solids exit through a 1.27 cm diameter polypropylene tube at the bottom of the column into a sealed bag. The sealed bag captures the solids and ensures that gas does not flow out the
bottom. The collection bag is in a cooled, insulated container to minimize sublimation of the solid components. More detailed diagrams of the gas-cooling tower and associated equipment appear in Appendix A.

A gas diffuser introduces cool gas containing the desublimating components, i.e., flue gas, at the bottom of the cooling tower. The gas diffuser includes 7 inlet holes. The breather inlet holes are centered 130.81 cm from the top edge of the assembled column.

4.2 Experimental Apparatus Computer User-Interface

Thermocouples for the cooling tower as well as the gas analyzer are interfaced with a computer through National Instruments field point modules and are controlled with LabVIEW 2010 software.

4.2.1 LabVIEW

Examples of the LabVIEW 2010 user interface appear in Appendix B. Table 4 lists the field points used in conjunction with LabVIEW 2010. The field point system is a remote input/output system designed to allow data acquisition and control. An RS-232 cable transmits the data digitally from the data acquisition system to the computer. Each FP-TC-120 module has built-in linearization and cold-junction compensation for the thermocouples.

<table>
<thead>
<tr>
<th>Field Point</th>
<th>Description/Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>FP-1000</td>
<td>Network Interface Module</td>
</tr>
<tr>
<td>FP-AI-110</td>
<td>Analog Input Module (gas Analyzer connection)</td>
</tr>
<tr>
<td>FP-TC-120</td>
<td>Thermocouple Module (8 channels/module, 2 modules)</td>
</tr>
</tbody>
</table>
4.2.2 Gas Analyzer

A Horiba PG 250 gas analyzer measures gas composition at the inlet and outlet, determining carbon capture effectiveness. Samples are collected along the side of the column through gas ports, which can be isolated using ball valves. The gas analyzer requires a flow rate of 400 cm$^3$/min. An internal pump within the unit maintains the flow rate.

4.3 Gas Pre-Cooler

A gas pre-cooler cools the inlet gas to a temperature much colder than ambient, but higher than its frost point. The gas pre-cooler consists of 366 cm of 0.635 cm diameter stainless steel tubing in a 7.62 cm diameter coil submersed in an ice bath. The ice bath consists of a mixture of liquid exchange fluid and CO$_2$ dry ice chips. Insulation surrounds the bath to minimize heat transfer with the surrounding environment. A diagram of the gas pre-cooler system can be found in Appendix A. The CO$_2$/N$_2$ gas mixture is supposed to be cooled from 296 K to 175 K using this apparatus. Thermocouples T14 and T13 monitor gas temperatures directly before and after the pre-cooler. Thermocouple T16 is placed within the ice bath and T15 measures ambient temperature.

4.4 Exchange Medium Reservoir

The exchange medium reservoir consists of a 10.16 cm diameter black pipe, 30.48 cm in length, which connects with a 10.16 to 3.81 cm bell reducing coupler. A 0.635 cm bushing is attached. A small section of pipe goes into a tee in which a ball valve is placed on the lower arm and a thermocouple is placed on the horizontal arm to measure the gas temperature within the reservoir. Thermocouple T1 is embedded within the reservoir to ensure that temperatures remain
below 135 K. Insulation and a 15.24 cm PVC pipe surround the reservoir to minimize heat transfer with the surrounding environment. Lead (2.159 mm diameter) spheres fill the reservoir. Over 34 kg are used in a single pass and are added to the reservoir as space becomes available.

Liquid N\textsubscript{2} is continuously added directly to the reservoir to cool the lead solid spheres. Evaporated N\textsubscript{2} acts as a blanket to minimize atmospheric water freezing on the particles. A diagram of the exchange reservoir cooler system appears in Appendix A. The exchange spheres are designed to cool from 296 K to 135 K using this system.
5 Results and Discussion

In order to accurately design a full-scale heat exchanger for the cryogenic carbon capture process understanding how initial conditions may effect temperature profiles and CO₂ capture is paramount. The following sections discuss a series of scenarios intended to illustrate anticipated temperature profiles and CO₂ capture efficiency trends for the column as they relate to initial inlet gas and particle temperatures, initial particle size, initial gas CO₂ concentration, mass ratio of particles to total gas stream, and height of the column. Only solid-particle results are included in this chapter.

Unless otherwise stated for a given scenario, the initial temperature of the exchange particle is 133K, the initial temperature of the gas is 175.15K, the initial concentration of CO₂ within the gas is 13.2 mole percent, the initial gas pressure is 1.0 bar, and the mass flow rate ratio of exchange spheres to gas is ~40.8. Calculations are based on 128 zones through a column with a radius of 0.635 cm. Position 0 is the top of the column -132.08 cm is the bottom of the column.

5.1 Model Initial Temperature Dependency

Initial gas and particle temperatures have an effect on the calculated gas temperature profile of the column. Figure 5-1 shows plots of column temperature as they relate to changes of
initial particle and gas temperatures. Initial gas temperatures of 175.15K and 181K with initial particle temperatures of 133K, 138K, and 143K are provided for comparison.

![Temperature Profile Graph](image)

Figure 5-1 Calculated Gas Temperature Profile vs Initial Particle and Gas Temperature using a lead-solid-core-exchange surface. Initial gas and particle temperatures vary from 175 to 181 K and 133, 138 to 143 K, respectively.

Results show that exit gas temperatures are similar to one another for a given initial particle temperature. It is theorized that the similarities are based on the extreme difference in magnitude of the mass of lead shot to desublimated CO\textsubscript{2} within the system. The initial difference between the two plots shows the dominance of desublimation that occurs towards the entrance of the gas within the column and dominance of only convection at the top of the column.

Particle temperature profiles versus initial gas and particle temperatures, as seen in Figure 5-2, show relatively minor dependency on gas temperature. This is explained by the residence time of a particle within the column as well as the amount of CO\textsubscript{2} desublimated versus the mass of the solid particle. The gas is in contact with the particle for only a short amount of time. Heat
transfer is dominated more by the heat-adsorbed from the desublimation of the CO₂ on the particles rather than the heat that is contributed by convection between the gas and the particles. This occurs close to the entrance of the gas within the column. Plots depicting changes in particle temperature as a function of column position for initial gas temperatures of 175.15K and 181K with initial particle temperatures of 133K, 138K and 143K are provided for comparison.

![Figure 5-2 Calculated Particle Temperature Profile vs Initial Particle and Gas Temperature using a lead-solid-core-exchange surface. Initial gas and particle temperatures vary from 175 to 181 K and 133, 138 to 143 K, respectively.](image)

As long as exchange media flow far exceeds the gas flow, the gas minimally affects the particle temperature profiles. The change in particle temperatures seen here is attributable to the rapid desublimation seen at the bottom of the tower as the gas first enters and the somewhat slower desublimation as the CO₂ concentration decreases higher in the column. The temperature
profiles of the particles will only continue to change significantly as long as there is CO\textsubscript{2} in the gas that can desublimate.

Initial gas and particle temperatures play parts in capture efficiency. As can be seen in Figure 5-3, which depicts the CO\textsubscript{2} capture efficiency of the various initial particle and gas temperature scenarios, the greater the initial particle temperature the lower the anticipated capture efficiency. Although the magnitude of capture efficiency is great due to the relative difference in the amount of CO\textsubscript{2} present to the amount of lead present, the trend is still notable.

![Figure 5-3 Calculated CO\textsubscript{2} Recovery vs Initial Particle and Gas Temperature using a lead solid core exchange surface](image)

**5.2 Model Initial Particle Size Dependency**

Initial particle size has an effect on the calculated gas temperature profile of the column. Figure 5-4 shows plots of the modeled column temperature profile for initial particle sizes of
0.15 cm, 0.2 cm 0.216 cm 0.25 cm, and 0.30 cm. Each run assumes the same gross volume of particles per time but simply given in different diameter particles. This means that for a given gross volume divided into particles there are more 0.15 cm particles than 0.30 cm particles that could be formed. A larger initial particle size translates into lower heat transfer surface area per volume and thus higher calculated gas temperatures and lower anticipated CO₂ recovery for the column.

![Figure 5-4](image)

**Figure 5-4 Calculated Gas Temperature Profile vs Initial Particle Diameter using a lead solid core exchange surface**

Particle temperature profiles versus initial particle diameter, as seen in Figure 5-5 for initial particle sizes 0.15 cm, 0.2 cm 0.216 cm 0.25 cm, and 0.30 cm, show similar particle temperature profiles. The slight difference seen is explained by the lower temperatures expected in the column as is illustrated in Figure 5-4 for smaller particles. The smaller particles have greater surface area for heat transfer for a given gross volume of particles.
The observed difference between CO₂ capture efficiencies is not significant until the fifth decimal place, which is beyond the expected precision of this model. This is due to the fact that the capture efficiency is related to a given volumetric flow of particles and not a single particle. This observed trend is relevant and included to demonstrate that capture efficiency is not enhanced by larger particles. Although, the actual CO₂ capture efficiency is relatively large it is anticipated that even for a lower ratios of exchange medium to CO₂ the same trend would be observed.

5.3 Model Initial Gas Concentration Dependency

Initial gas composition has only a slight effect on the calculated gas temperature profile of the modeled column. This is due to the large mass ratio of particles to gas, which causes
convection to be the primary contributor for heat transfer. Figure 5-7 explores the different gas column temperature profile as related to initial gas concentrations of 0.1, 0.5, 1, 5, 10 and 13.2 mole percent CO₂.

It is reasonable that convective heat transfer dominates within this described system. The thermal conductivity of N₂ (the primary gas component) is nearly double that of CO₂ at the operating conditions of the cooling tower.

Particle temperature profiles vs initial CO₂ gas concentration, as seen in Figure 5-8, show that the majority of the desublimation occurs near the gas entrance or bottom portion of the column. This could indicate that shorter columns may be more efficient than taller, more
expensive columns for high exchange media mass to gas ratios. As the ratio of exchange media to gas is decreased, it is anticipated that the required column height may increase. However, the capital cost versus operational cost would differ significantly for this sort of system. Savings from decreased exchange media handling would likely make a taller column more economical.

Initial CO₂ concentration does affect capture efficiencies. Figure 5-9 shows a plot of anticipated recovery for a given initial CO₂ mole concentration. When more CO₂ is present, a greater amount of CO₂ will desublimate sooner within the column, which implies that the overall column temperature will decrease sooner. A faster temperature drop will result in greater capture efficiencies in full-scale production facilities as well.
Figure 5-8 Calculated Particle Temperature Profile vs Initial CO$_2$ Gas Concentration using a lead solid core exchange surface

Figure 5-9 CO$_2$ Recovery vs Initial CO$_2$ Gas Concentration using a lead solid core exchange surface
5.4 Model Initial Mass Ratio Dependency

The mass flow rate ratio of exchange spheres to gas effects the calculated gas temperature profile of the column, as can be seen in Figure 5-10. This is reasonable in that even though a lower ratio may have a greater number of moles of CO\textsubscript{2} available for desublimation it also has a greater amount of N\textsubscript{2} which will contribute to convection heat transfer which will cause the particles to heat up more than otherwise. Plots of various initial exchange to gas mass ratio, including 10:1, 15:1, 20:1, 25:1, 30:1, 35:1, and the comparison ratio ~40.8:1 (41:1) are given.

![Calculated Gas Temperature Profile vs Initial Exchange to Gas Mass Ratio](image)

Figure 5-10 Calculated Gas Temperature Profile vs Initial Exchange to Gas Mass Ratio using a lead solid core exchange surface

The particle temperature profiles versus initial exchange to gas mass ratio as seen in Figure 5-11 again shows that the majority of the desublimation occurs near the gas entrance or bottom third of the column, as indicated by the change in slope that occurs. A lower ratio leads to
a higher average gas temperature, which means that CO₂ capture efficiency will likely decrease as the mass ratio decreases.

![Graph showing calculated particle temperature profile vs initial exchange to gas mass ratio using a lead solid core exchange surface.](image)

**Figure 5-11 Calculated Particle Temperature Profile vs Initial Exchange to Gas Mass Ratio using a lead solid core exchange surface**

Initial mass ratio could play a vital part in capture efficiency. However, results were not readily meaningful until the $10^{-5}$ decimal place, which is outside the precision this model can reasonably predict. As can be observed in Figure 5-12, the CO₂ recovery is relatively the same for the ratios studied. Below 10:1 effects of the column design came into play in that entrainment of the particles was beginning to cause destabilization within the model. Solids handling will act as an energy sink within the process and the smaller the ratio possible the better the economic outlook of this process.
There is a point in which building a bigger column will have little effect on capture efficiencies. The current parameters of the model, based on the experimental apparatus, show that capture efficiency increases only slightly beyond 25 cm for the flow rates given. This is shown in Figure 5-13, which shows a plot the expected capture efficiency versus column height. It is recognized that at shorter columns do not provide enough residence time for desublimation to be complete. At greater than 5 cm convection dominates heat transfer of the particle.
5.6 Experimental Results

Experimentation was able to show that CO$_2$ will desublimate upon a cold falling spherical particle. However, experimentation was unable to verify or refute the models’ accuracy. Several challenges in testing occurred and are being worked on by others within the research group at Brigham Young University.

Desublimation occurred on the particles. Visual inspection of the particles, post processing, shows sublimation of the collected CO$_2$ in the atmosphere when the particles were no longer in a sealed container. This can be seen in Figure 5-14.

Figure 5-13 Calculated CO$_2$ Recovery vs Column Height using a lead solid core exchange surface
The Horiba Gas analyzer was used to determine CO$_2$ concentration within the gas stream. Concentration of the CO$_2$ within the gas went from 13.2% to as below 2%. The overall ice buildup on the particles was relatively small in comparison to the total particle mass unless the CO$_2$ in the collection bag sublimated and flooded the column with CO$_2$ gas. This can be observed in Figure 5-15.

The amount of CO$_2$ recovered versus the temperature difference between the recorded reservoir temperature and the temperature of the gas at 128.0 cm from the top of the column is depicted in Figure 5-16. The general trend shows that initial lower temperature differences between the inlet gas and the exchange fluid surface provide better CO$_2$ capture efficiency.
Figure 5-15 Image showing Dry Ice Build Up on Underflow Particles From the Falling Sphere Heat Exchanger Column

Figure 5-16 Graph depicting experimentally obtained CO₂ recovery versus initial temperature difference between the incoming particle and incoming gas streams
Experimental work (conducted by Bradley Nielson and Dave Frankman) undertaken with the apparatus shows promising results. Figure 5-17 illustrates that the majority of the CO$_2$ capture occurs near the gas inlet. In agreement with model predictions, there is relatively little change in CO$_2$ concentration between the bottom third of the column to the mid-section of the apparatus.

Figure 5-17 Experimentally obtained CO$_2$ concentrations at the inlet, 1/3, and midpoint positions over time. (Data collected by Bradley Nielson and Dave Frankman)
6 Conclusions and Recommendations

The model predicts that a falling sphere heat exchanger can be used to help capture CO$_2$ within the CCC process. Due to experimental design constraints of using a solid sphere of vastly differing molecular weight (ie. exchange $\sim$207 gm/mol, initial gas mixture $\sim$30 gm/mol) and density the model predicts high capture efficiencies. This means that for a given mole ratio there is far more lead at the end of the pipe than captured CO$_2$. As CO$_2$ is not in the system in a great enough quantities to truly affect the column bulk and particle temperatures this is still a subject of discussion. Even so, the relationships that are presented can be used within either liquid spray tower systems or a system of modified geometry.

The model is limited by the fact that the majority of the properties used to calculate heat transfer are at film temperature. For laminar conditions and a well-behaved boundary layer this should not be a problem for the heat transfer characteristics described. Within the present specifications, the film temperature is very close to the point in which desublimation can occur for a system that has initial temperatures of 133K for exchange medium and 175.15K for gas. This means that, for the given flow rates used for experimentation, most if not all the desublimation occurs close to the entrance of the gas and the rest occurs before exit. Furthermore, the model is limited by the iterative nature of the calculations. A good initial guess is needed to help ensure the model converges quickly and does not lose stability. Under relaxation methods employed have enhanced stability.
It is felt that a liquid exchange medium would have differing results and would show a greater temperature drop from one end of the column to the other. This is observable in that if flow rates of the gas are raised too great then the particles become entrained and the model loses stability. The model can only be valid if the flow rate of the exchange medium allows at least one particle to be present. Fraction of particles would be calculable but would not be realistic.

General trends that are observable for the given set of conditions indicate that a sweet spot exists in heat exchanger design. As the majority of desublimation occurs within the first few nodes care must be given to ensure that unneeded cooling of a lean CO₂ mixture is undertaken. Particle diameter and initial CO₂ concentration both play an important part in overall CO₂ capture efficiency. Higher initial CO₂ concentration and smaller particle diameter seem to enhance CO₂ recovery. Furthermore, initial gas and particle temperatures play an important part in CO₂ capture efficiency. Lower initial temperatures indicate the potential for greater CO₂ capture.
7 References


Appendix A.  P&ID Falling Drop Heat Exchanger

Process and instrumentation diagrams for the heat exchanger are given. Figure A-1 represents the Gas Pre-Cooler, Figure A-2 represents the Cooling Tower, and Figure A-3 represents the Exchange Media Reservoir/Cooler.
Figure A-1 Gas Pre-Cooler P&ID
Figure A-2 Cooling Tower P&ID
Figure A-3 Exchange Media Reservoir/Cooler P&ID
Appendix B. LabVIEW Programming

The LabVIEW 2010 program is a modified version of programming by Darren Cundick and other students from BYU. All FP-TC-120 modules are added as arrays using I/O device interfaces. Figure B-1 represents the desktop version of the LabVIEW 2010 VI program.

Figure B-1 LabVIEW Program Desktop
Appendix C. Relationships Used

7.1 Film Temperature

\[ T_f = \frac{1}{2} T_g + T_s \]

7.2 Molecular Weight

The molecular weight of the gas and particle mixtures (Turns 2000):

\[ MW_{mix} = \sum_i y_i MW_i \]

7.3 Mole Fraction

The mole fractions of the gas and particle mixtures:

\[ y_i = \frac{n_i}{\sum_i n_i} \]

7.4 Density

7.4.1 Liquid Density

Liquid density of the exchanger fluid (Rowley, Wilding et al. 2006):

\[ \rho_l = \frac{A}{B^{1+\frac{1-T/\theta}{C}} D} \]
7.4.2 Solid Density

Density of the solid CO$_2$ (Rowley, Wilding et al. 2006):

$$\rho_{CO_2,s} = A + BT + CT^2 + DT^3 + ET^4$$

7.4.3 Particle Density

$$\rho_p = \rho_{CO_2,s}x_{CO_2} + \rho_lx_{exc}$$

7.4.4 Gas Density

Density of the gas is given by the ideal gas law:

$$\rho_g = \frac{p_{total}M_{W_{mix,g}}}{R_gT}$$

7.5 Vapor Pressure

7.5.1 Solid CO$_2$

Vapor Pressure (Rowley, Wilding et al. 2006):

$$p_{vap} = e^{A + \frac{B}{T} + C\ln T + DT^E}$$

7.5.2 Exchange Fluid

Vapor Pressure (Rowley, Wilding et al. 2006):

$$p_{vap} = A + BT + CT^2 + DT^3 + ET^4$$
7.6 Geometry

7.6.1 Particle Diameter

\[ d_p = \frac{6}{\pi} \frac{\pi}{6} \left( d_{p_{i-1}} \right)^3 + \frac{n_i - n_{i-1}}{\rho_{p_{i,j}}} \] ^{1/3}

7.6.2 Particle Surface Area

\[ SA = \pi d_p^2 \]

7.6.3 Total Surface Area

\[ SA_{total} = j t_{p_{i,j}} SA \]

7.7 Gas Viscosity

7.7.1 Lennard Jones Parameters

\[ \mu = \frac{5}{16} \frac{\overline{MT}}{\sigma^2\Omega_\mu} \]

7.7.2 Collision Integral

\[ \Omega_\mu = \Omega_k = \frac{1.16145}{T^{0.14874}} + \frac{0.52487}{e^{0.77320T}} + \frac{2.16178}{e^{2.437870T}} \]
7.7.3 $T^*$

$$T^* = \frac{kT}{\varepsilon}$$

7.7.4 Gas Mixture Viscosity

$$\mu_{mix} = \prod_{\alpha=1}^{N} \frac{x_\alpha \mu_\alpha}{\beta \times \Phi_{\alpha \beta}}$$

7.7.5 Dimensionless $\Phi_{\alpha \beta}$

$$\Phi_{\alpha \beta} = \frac{1}{8} \left( 1 + \frac{M_\alpha}{M_\beta} \right)^{-1/2} \left( 1 + \frac{\mu_\alpha}{\mu_\beta} \right)^{1/2} \left( \frac{M_\alpha}{M_\beta} \right)^{1/4}$$

According to Curtis and Hirschfelder, as cited in Bird et al., the above relationship “has been shown to reproduce measured values of the viscosities of mixtures within an average deviation of about 2%”

7.8 Thermal Conductivity

7.8.1 Thermo Conductivity of the Gas

(Rowley, Wilding et al. 2006)

$$k = \frac{AT^B}{1 + \frac{C}{T} + \frac{D}{T}}$$
7.8.2  Gas Mixture Thermo Conductivity

(Bird, Stewart et al. 2002)

\[ k_{\text{mix}} = \frac{N}{\alpha=1} \frac{\chi_{\alpha}k_{\alpha}}{\beta \chi_{\beta} \Phi_{\alpha\beta}} \]

The coefficient \( \Phi_{\alpha\beta} \) is identical for both viscosity and thermal conductivity equations. Comparisons with experimental data by Mason and Saxena as described in Bird, Stewart, and Lightfoot indicate “an average 4% deviation for mixtures containing non-polar-polyatomic gases such as \( \text{O}_2, \text{N}_2, \) and \( \text{CO} \)” (Bird, Stewart et al. 2002)

7.8.3  Thermo Conductivity of the Exchange Fluid

(Rowley, Wilding et al. 2006)

\[ k = A + BT + CT^2 + DT^3 + ET^4 \]

7.8.4  Thermo Conductivity of the Particle

(Rowley, Wilding et al. 2006)

\[ k_{\text{mix},p} = \frac{\sum_{i} x_{i}k_{i}}{i} \]
7.9 Diffusion Coefficient

7.9.1 Diffusion Coefficient – $ab$

\[
D_{ab} = 0.0018583 \times T^3 \frac{1}{M_A} + \frac{1}{M_B} \frac{101325}{p\sigma^2\Omega_{D_{AB}}}
\]

where $D_{ab}$ has units of cm$^2$/s, $\sigma_{ab}$ is has units of Angstrom, Å, $T$ is in Kelvins, and $p$ is has units of Pa.

7.9.2 Effective Diffusion Coefficient – a-mix

(Wilke 1950; Richard 1996)

\[
D_{ab} = D_{1,\text{mix}} = \frac{1}{\frac{y'_2}{D_{1,2}} + \frac{y'_3}{D_{1,3}} + \cdots + \frac{y'_n}{D_{1,n}}}
\]

7.9.3 $y'$

\[
y'_n = \frac{y'_n}{y_2 + y_3 + \cdots + y_n}
\]

7.10 Dimensionless Numbers

(Bird, Stewart et al. 2002; White 2003)
7.10.1 Reynolds

\[ Re = \frac{d_p \rho_g v_g - v_p}{\mu_g} \]

7.10.2 Prandtl

\[ Pr = \frac{C_p \mu}{k} \]

7.10.3 Schmidt

\[ Sc = \frac{\mu_g}{\rho_g D_{ab}} \]

7.10.4 Biot Heat

\[ Bi = \frac{\Box_m \frac{1}{6} d_p}{k_p} \]

7.10.5 Biot Mass

\[ Bi_m = \frac{k_{xm} \frac{1}{6} d_p}{D_{ab}} \]

7.11 Transfer Coefficients

(Bird, Stewart et al. 2002)
7.11.1 Heat

\[ \Theta_{m} = \frac{N u_{m} k}{d_{p}} \]

7.11.2 Mass

\[ k_{xm} = \frac{c D_{ab} S \Theta_{m}}{d_{p}} \]

where \( D_{ab} \) is the effective diffusion coefficient.

7.12 Blowing Factor

(Bird, Stewart et al. 2002)

\[ \theta_{m} = \ln \left( \frac{1 + R}{R} \right) \]

where

\[ R = \frac{W_{ao} + W_{bo} - \frac{p_{vap,A}}{P_{total}} x_{A} - x_{A}^{\infty}}{W_{ao} - \frac{p_{vap,A}}{P_{total}} W_{ao} + W_{bo}} \]

7.13 Heat Capacity

7.13.1 Gas

\[ C_{p,i,g} = AT^{-2} + B + CT + DT^{2} \frac{R_{g}}{R} \]
7.13.2 Gas Mixture

\[ C_{p,ave,g} = \sum_i y_i C_{p,i,g} \]