AN AMBIENT-PRESSURE ABSORPTION HEAT PUMP USING MICROPOROUS MEMBRANES: DESIGN, MODELING, AND EXPERIMENTAL INVESTIGATION

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The final copy of this thesis has been examined by the signatories, and we Find that both the content and the form meet acceptable presentation standards Of scholarly work in the above mentioned discipline Woods, Jason David (Ph.D., Mechanical Engineering)

An ambient-pressure absorption heat pump using microporous membranes: design, modeling, and experimental investigation

Thesis directed by Research Professor John Pellegrino

A membrane absorption heat pump uses absorbent (a salt solution) and refrigerant (water) flows separated by a membrane to create a temperature difference, or temperature lift, used for heating or cooling. Compared to conventional absorption heat pumps, an ambient-pressure membrane heat pump is built from simpler, more compact, and potentially less expensive components. Storing the absorbent in an unpressurized tank offers unique options for thermal energy storage for solar heating and cooling of buildings and potential applications in long-distance thermal energy transport.

The contributions of this thesis can be summarized as: (1) design characterization of this novel process, focusing on controlling the heat and mass transfer in a membrane device for energy storage and transport applications, (2) modeling the process, including detailed analyses of the transport phenomena and a generalized analysis of membrane pore-size distribution, which is applicable to a wide range of membrane processes, and (3) experimental characterization of this process, with validation of the model.

Results from a first-principles numerical model shows that using a 1-mm air gap between two membranes gives temperature lifts four times higher than using a single membrane with no air gap. Predicted temperature lifts for the air-gap design range from 5-25°C, with higher inlet temperatures giving higher temperature lifts. Experimentally measured temperature lifts over a range of flow rates, salt mass fractions, and temperatures match the modeling within 15% with

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an R^2 of 0.91. The maximum temperature lift achieved was 9°C, but temperature lifts up to 20°C are anticipated with a future design using more porous hollow fibers.

The detailed analyses of the transport phenomena led to the following conclusions. First, natural convection in the air gap is negligible for the geometries considered here. Second, the membrane's porosity, tortuosity factor, and pore size are adequate to predict membrane mass transfer coefficients, with pore-size distribution having a minimal effect. Third, an accurate estimate of the membrane's effective thermal conductivity is unimportant for modeling a membrane heat pump. Fourth, most of the complex phenomena occurring in the boundary layers are unimportant for predicting the Nusselt and Sherwood numbers for the flows. Experiments on the three prototypes reinforce these conclusions.

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Nomenclature

Α	surface area, radiation (m^2) ; area available for heat and/or mass transfer (m^2)
a_{w}	water activity
a _s	water activity of absorbent solution
\mathbf{B}_0	lumped parameter in Eq. (3.7)
Br	Brinkman number
c _p	specific heat capacity $(J kg^{-1}K^{-1})$
$d_{\rm gap}$	air-gap width (m)
d _h	hydraulic diameter (m)
di	hollow fiber inner diameter (m)
d _o	hollow fiber outer diameter (m)
$d_{ m p}$	membrane mean pore diameter (m)
D	lumped parameter in radiation analysis, $D = d_o / t$
D_{12}	molecular diffusion coefficient ($m^2 s^{-1}$)
D_{sw}	molecular diffusion coefficient for salt in aqueous salt solution (m ² s ⁻¹)
$D_{\rm va}$	molecular diffusion coefficient for water vapor in air $(m^2 s^{-1})$
D_{M}	effective transport coefficient for molecular (ordinary) diffusion $(m^2 s^{-1})$
D_{K}	effective transport coefficient for Knudsen flow $(m^2 s^{-1})$
$D_{ ext{K-M}}$	effective transport coefficient for combined Knudsen-molecular diffusion (m 2 s $^{-1}$)
$D_{ ext{K-V}}$	effective transport coefficient for combined Knudsen-viscous flow $(m^2 s^{-1})$
$D_{ m V}$	effective transport coefficient for viscous flow, $\kappa p/\eta$ (m ² s ⁻¹)
F ₁₋₂	radiation view factor from surface 1 to surface 2
g	acceleration due to gravity (m s^{-1})

Gr	Grashof number
Gz_x	Graetz number based on length <i>x</i>
Н	half-channel height (scaling analysis) (m)
H _{channel}	channel thickness (m)
$h_{ m i}$	heat transfer coefficient of region i (W m ⁻² K ⁻¹)
H_v	enthalpy of vapor (J kg ⁻¹)
ΔH_{vap}	enthalpy of vaporization (J kg ⁻¹)
ΔH_{mix}	enthalpy of mixing (J kg ⁻¹)
J	mass flux (kg $m^{-2}s^{-1}$)
Κ	overall mass transfer coefficient (kg m ⁻² s ⁻¹ kPa ⁻¹)
K_0	mass transfer coefficient not including polarization effects (kg m ⁻² s ⁻¹ kPa ⁻¹)
Ki	mass transfer coefficient of region i (kg m ⁻² s ⁻¹ kPa ⁻¹)
k _m	convective mass transfer coefficient (m s ⁻¹)
Kn	Knudsen number
L	length of module (m)
М	molecular mass (kg kmol ⁻¹)
ṁ	mass flow rate
n _i	mass flux of component i (kg m ⁻² s ⁻¹)
N _{fibers}	number of hollow fiber membranes in each row of the module
N _{nodes}	number of nodes in one direction of finite-difference model
$N_{ m rows}$	number of rows in module
NTU	non-dimensional number of transfer units for membrane heat pump, used instead of
	NTU _{dim}

NTU _{dim}	dimensional number of transfer units for membrane heat pump, not used (kPa K ⁻)	
Nu	Nusselt number	
р	pressure (kPa)	
Pe	Peclet number	
p_i	partial pressure of component <i>i</i> (kPa)	
q''	heat flux (W m ⁻²)	
Q	heat flow (W)	
Q_{prod}	heat pump productivity (W m ⁻² kPa ⁻¹)	
R	universal gas constant (8314 J mol ⁻¹ K ⁻¹)	
$R_{\rm c}$	heat capacity ratio	
Pr	Prantdl number	
Ra	Rayleigh number	
Re	Reynolds number	
S	conduction shape factor (m^{-1})	
\mathbf{S}_0	lumped parameter in Eq. (3.7)	
Sc	Schmidt number	
Sh	Sherwood number	
Sp	Sparrow number	
t	time; fiber pitch (distance between hollow-fibers within a row) (m)	
Т	temperature (K or ^o C)	
$\Delta T_{ m lift}$	temperature lift (difference between outlet solution temperature and inlet water	
	temperatures (K))	
ΔT_{∞}	asymptotic temperature lift (K)	

NTU_{dim} dimensional number of transfer units for membrane heat pump, not used (kPa K⁻¹)

и	x-direction velocity (scaling analysis) (m s ⁻¹)	
U	overall heat transfer coefficient (W m ⁻² K ⁻¹)	
U_0	heat transfer coefficient not including polarization effects (W $m^{-2}K^{-1}$); inlet velocity	
	(scaling analysis) (m s ⁻¹)	
V	y-direction velocity (scaling analysis) (m s ⁻¹)	
$V_{ m wall,0}$	wall velocity at module inlet (scaling analysis) (m s ⁻¹)	
W	width of module (m)	
x	coordinate along flow direction	
X _i	mass fraction of component <i>i</i>	
У	coordinate perpendicular to flow channels; coordinate perpendicular to the wall	
<i>Yi</i>	mole fraction of component <i>i</i>	
Z.	coordinate in line with flow channels, perpendicular to flow direction	
Z.	spacing between rows of hollow fibers	
Greek letters		
α	thermal diffusivity, $\rho c_p / k \ (m^2 s^{-1})$	
β	thermal expansion coefficient (K ⁻¹)	
$\beta_{\scriptscriptstyle M}$	solutal or concentration expansion coefficient	

$\delta_{ m mem}$	membrane thickness (m)	
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- $\varepsilon_{\rm HP}$ membrane heat pump effectiveness
- $\varepsilon_{\rm HX}$ heat exchanger effectiveness
- $\varepsilon_{\rm rad}$ radiative emissivity
- η membrane heat pump efficiency

γ	surface tension (N/m)
λ	thermal conductivity (W $m^{-1}K^{-1}$)
П	dimensionless group
ρ	density (kg m ⁻³)
μ	dynamic viscosity (kg m ⁻¹ s ⁻¹)
V	kinematic viscosity $(m^2 s^{-1})$
$\sigma_{_{SB}}$	Stefan-Boltzmann constant $(5.67 \times 10^{-8} \text{ W m}^{-2} \text{K}^{-4})$
τ	membrane tortuosity factor
ω_{s}	salt mass fraction
subscripts	
0	inlet value (scaling analysis)
1, 2	components
abs	absorber
avg	average
b	bulk flow
cond	condenser
eff	effective
exp	experimentally-measured value
evap	evaporator
g	vapor-air mixture in the gap or in the membrane pores
gap	air gap

gen generator

HX parameter used in heat exchanger design

HP	parameter used in membrane heat pump design			
∞	far-field condition (scaling analysis)			
LM	log-mean average or log-mean difference			
М	concentration; species equation (scaling analysis)			
m	membrane-liquid interface			
mem	membrane			
model	calculated result from model			
N2	nitrogen			
polymer	property of solid membrane material			
ref	reference value (scaling analysis)			
S	absorbent solution; scale factor (scaling analysis)			
sat	saturated liquid-vapor condition			
Т	thermal; energy equation (scaling analysis)			
v	vapor			
w	water			
wall	y-direction value at the membrane surface (scaling analysis)			
abbreviations				
AMT	Applied Membrane Technology, Inc.			
CaBr ₂	calcium bromide			
CaCl ₂	calcium chloride			
Ca(NO ₃) ₂	calcium nitrate			
CFD	computational fluid dynamics			
EES	engineering equation solver (computer program)			

ERV	energy recovery ventilator
H_2O	water
HVAC	heating, ventilation, and air conditioning
IEA	International Energy Agency
LiCl	lithium chloride
LiBr	lithium bromide
MD	membrane distillation
MgCl ₂	magnesium chloride
N_2	nitrogen
NH ₃	ammonia
NREL	National Renewable Energy Laboratory
NTU	number of transfer units
OLI	electrolyte software company (not actually an abbreviation)
PCM	phase change material
PP	polypropylene
PTFE	polytetrafluoroethylene
SEM	scanning electron microscope
ZnCl ₂	zinc chloride

CHAPTER 1 Introduction

The primary objectives of this research are to design, model, and test a membrane-based absorption heat pump that operates at ambient pressure. A theory on absorption heat pumps operating at ambient temperature has not been developed prior to this thesis. Although the use of membranes in absorption heat pumps has been investigated before (e.g., [1-3]), the focus there was on conventional heat pumps that operate far from ambient pressure (either on the order of 0.01 atm or 5 atm). The membrane heat pump discussed here operates at ambient pressure; the non-condensable gases are not removed from the system. This is not inherently better than the conventional method, but it provides one key advantage: the system's components, such as valves, pumps, storage vessels, and pipes, do not need to withstand high pressure differences and are thus simpler, lighter, and likely less expensive. This advantage also facilitates using an absorption heat pump's working fluid to store or transport thermal energy; it can now be stored or pumped at ambient pressure.

An ambient pressure membrane heat pump is a novel process. This thesis conceptualizes this process, with a focus on controlling the heat and mass transfer in a membrane device for unique energy storage and transport applications. It characterizes the design, the operating strategies, and the performance of a membrane heat pump. It does this with a newly created model of the device that considers the details of the complex geometry and complex transport phenomena. To verify this modeling, prototypes were constructed and tested for select device designs and a range of operating conditions. As part of the modeling process, this research also develops a novel method for analyzing and presenting the effects of pore size distribution in microporous membranes, which is applicable to a wide range of membrane processes.

These contributions can be summarized as follows: (1) design characterization of this novel device and process, (2) modeling of this process, which includes detailed analyses of each transport phenomena and a generalized analysis of membrane pore size distribution, and (3) experimental characterization of this process, with a validation of the model. Figure 1.1 shows how these three topics are related. Each topic is discussed in more detail in the second half of this Introduction chapter. They are then the focus of Chapter 3, Chapters 4 and 5, and Chapter 6, respectively. First, though, this membrane heat pump process is described in more detail.



Figure 1.1: Design, modeling, and experimental approach for the membrane heat pump. Designs are evaluated with modeling, with final designs selected for prototype construction and experiments. These experiments validate the modeling approach.

1.1 Concept introduction: An ambient-pressure membrane heat pump

A membrane heat pump, as defined here, is actually only a portion of an absorption heat pump. Specifically it is the evaporator and the absorber in an absorption heat pump. Chapter 2 discusses these two components for conventional absorption heat pumps, along with the other two components: the generator and the condenser. The focus of this thesis is on the combined absorber-evaporator component.

To illustrate the membrane heat pump concept, consider it as a part of a building heating system. An intermittent heat source, such as solar or waste heat, is supplied to an aqueous salt solution, boiling off pure water and increasing the concentration of the salt. This higher concentration lowers the water activity, increasing its potential to absorb water vapor. The concentrated solution stores this potential until the building needs to be heated. At this point, the concentrated solution flows into the membrane heat pump component, where the solution flows over a microporous membrane, behind which is water (Figure 1.2). Both liquids enter at ambient temperature and pressure. The low activity of the salt solution attracts water vapor, causing it to evaporate on the water side of the membrane, travel through the membrane pores as vapor, and condense on the salt solution side of the membrane. The membrane is hydrophobic to prevent liquids from passing through the pores. Evaporation cools the water as condensation heats the solution, creating a temperature difference. This temperature difference, or temperature lift, is used to heat the building. The 'heat pumping' is the transfer of heat from the low-temperature water channel to the high-temperature solution channel. In the terminology of conventional absorption heat pumps, the water channel is the evaporator and the salt-solution channel is the absorber.

The 'membrane' in a membrane heat pump deserves some additional attention. It is not simply a membrane, but two membranes with an air gap in between (Figure 1.3). The air gap provides a low resistance to vapor transport (latent energy), but a high resistance to heat conduction (sensible energy). This ratio of latent to sensible energy transfer is critical to improving the membrane heat pump's performance. Constructing this membrane-air-gap composite is difficult without a structure of some kind in the air gap to support the pressuredriven liquid flows. But an air gap support decreases the available area for vapor transfer and most likely increases sensible energy transfer, as thermal conductivities of most solid materials are greater than air's. Designing this membrane-air-gap composite to minimize heat transfer and maximize mass transfer is the primary focus of designing the membrane heat pump.



Figure 1.2: Schematic of heat pump, showing upward-flowing absorbent (in this study, an aqueous salt solution) and a downward-flowing refrigerant (in this study, water). The temperature variation along the flow direction (x) is shown to the right.



Figure 1.3: Heat and vapor flows between the two streams in the membrane heat pump. T(y) is the temperature profile between the two flows, $p_v(y)$ the vapor pressure profile, and $\omega(y)$ is the profile of the salt mass fraction between the bulk flow and the membrane surface.

1.2 Design

Membrane heat pump design refers primarily to (1) selecting and building the device geometry, (2) selecting the absorbent, and (3) developing a method to measure heat pump performance. Chapter 3 discusses the design approach, which results in potential designs, some of which are selected for experimental prototypes (Figure 1.1). The model, discussed in the next section, is used to compare and select the near-optimal designs.

1.2.1 Selecting device geometry

Three choices for the heat pump design are important: flow direction, membrane type, and module layout. The direction of the two flows can be co-current, counter-current, or crosscurrent. Some of these flow-direction configurations perform better than others, but some are more difficult to physically construct. The two common membrane types, and the two considered in this thesis, are flat-sheet membranes, which are porous sheets about the thickness of paper, and hollow-fiber membranes, which are small tubes (less than 1 mm diameter) with porous walls. Associated with these membrane types is the module layout, such as shell-and-tube or plate-and-frame. The module layout not only affects performance, but also dictates how the membrane-air-gap composite is formed, as discussed in detail in Chapter 3.

1.2.2 Selecting the absorbent

There are many tradeoffs in selecting the absorbent, some of which are more important here than for conventional absorption heat pumps. The most important property is the vapor pressure reduction of the absorbent (the water activity). Tied to this is the absorbent's solubility since higher concentrations lead to lower water vapor pressures. However, the absorbent itself should have a high vapor pressure such that water vapor is the only component transferred across the membrane.

Considerations with particular importance for the membrane heat pump are the viscosity and the cost. Viscosity is important for thermal energy transport applications, where the absorbent is pumped long distances. Cost is an important factor for storage applications, where large amounts of the absorbent are stored in tanks. Section 3.2.1 discusses the important

absorbent properties in more detail, while Section 5.3.2 presents how the properties of different absorbents affect heat pump performance.

1.2.3 Characterizing each design

In this thesis, the term characterizing refers to quantitatively describing the design, the operating conditions, and the performance of a membrane heat pump. The design goal is to maximize the ratio of latent to sensible energy transfer, but there is a tradeoff between this ratio and the initial cost and size of the device. This tradeoff is characterized with a productivity-selectivity plot, similar to a plot used for membrane separation processes. The operating conditions are characterized synonymously to heat exchangers by using a modified NTU and a heat capacity rate ratio, which is the ratio of the flow-weighted heat capacities of the two liquids.

After characterizing the design and the operating conditions, the performance of the heat pump must be measured. What is performance? An intuitive choice is the temperature lift, which is the difference between the outlet solution temperature and the inlet water temperature. And then one must evaluate the design thermodynamically. Conventional absorption heat pumps are evaluated with the coefficient of performance, or COP. But defining a COP requires knowledge of the overall cycle and the application. Instead, a general approach is taken here that focuses on the 'efficiency' of the absorption process in the membrane heat pump. There is also a tradeoff between the efficiency and the temperature lift, but it depends on flow rates and not the physical design. Changes in the design generally increase or decrease both efficiency and temperature lift together. Exceptions are multi-stage and multi-effect designs, but these are not discussed in depth in this thesis. All of these performance metrics are discussed in Section 3.3.

1.3 Model

Chapter 4 describes a detailed finite-difference model and the methods for estimating the transport coefficients of the membrane, air gap, and internal boundary-layer flow (see Figure 1.3). The model compares the performance between the different designs discussed in the previous section, and compares the performance for different flow rates, inlet temperatures, and salt mass fractions. The goal in modeling the membrane heat pump is to accurately predict experimental temperature lifts with the simplest possible model. Keeping the model simple keeps runtime low. This is important to perform all the runs required for parametric, sensitivity, and uncertainty analyses. But there is a tradeoff between accuracy and simplicity. Chapter 4 analyzes the various simplifying assumptions made in the model. The main questions to answer are:

- 1. What parameters are required to accurately predict the heat and mass transfer coefficients of the membrane?
- 2. Do conduction and diffusion equations adequately model the air gap? Or does the model need to consider natural convection?
- 3. What is the effect of the transverse mass flux from the wall on the development of the thermal and concentration boundary layers? Are there any other important phenomena in the flows that affect heat and mass transfer?

These three questions are answered with scaling arguments and sensitivity analyses in Chapter 4, and are reinforced by experimental data in Chapter 6. With these assumptions, the modeling results are presented in Chapter 5 to compare the performance of different module designs. In particular, it looks at the theoretical benefit of using an air gap, and it compares different prototype designs. Chapter 6 then compares the model and experimental results of the designs selected for the prototypes.

1.4 **Experiments**

Experiments performed on a few selected designs are compared to the model-calculated results to validate the model and to answer the question above about natural convection in the air gap. The calculated parameters are the overall mass transfer coefficient, the overall heat transfer coefficient, and the temperature lift. The measured parameters are the mass flux across the membrane, the temperatures, and the flow rates. For the mass-flux measurement, the most difficult here, two scales measure the change in mass of reservoirs containing the absorbent solution and the refrigerant water. Measuring mass directly instead of volume eliminates the need for temperature compensation. Chapter 6 presents the experimental methods in more detail, discusses the experimental results, and compares the experiments with the modeling results of Chapter 5.

CHAPTER 2 Background and literature review

This chapter provides background on three fields relevant to this thesis: absorption heat pumps, membrane processes, and thermal energy storage and transport. The primary purpose here is to put the work in this thesis in context. Literature is also cited throughout this thesis as it pertains to the content in each chapter.

2.1 Absorption heat pumps

This section introduces absorption heat pumps to readers unfamiliar with the topic. Those uninterested in background information on absorption heat pumps can skip to Section 2.2. There are three topics to understand about absorption heat pumps: its temperature levels, its working fluids, and its cycle,

2.1.1 Absorption heat pump temperature levels

Heat pumps move heat from a low temperature to a higher temperature with an input of either work or heat. Most commonly, this input is electrical work supplied to a compressor as in a vapor compression heat pump. But in an absorption heat pump, this input is thermal energy at a third higher temperature. The high temperature reservoir is a heat source, such as a natural gas boiler, which supplies heat (Q_H) at the high temperature. There are thus three temperature levels in an absorption heat pump process: high (H), intermediate (I), and low (L). The heat is input at the high and low temperature reservoirs, and output at the intermediate temperature reservoir (Figure 2.1). Two examples make this clearer. In one configuration, the low-temperature reservoir is the ambient, which supplies heat (Q_L) to the heat pump. The heat pump releases heat at the intermediate level (Q_I), which can be used to heat a building. This intermediate energy transfer is the sum of the heat input at the high temperature (Q_H) and the low temperature (Q_L),

and thus more energy is supplied than is input as fuel (Q_H) . In the second example, heat is still discharged to the intermediate temperature reservoir, but this time this reservoir is the ambient. The low-temperature reservoir is the building, which 'inputs' heat at this low temperature; the heat pump cools the building. Thus absorption heat pumps can be used for both heating and cooling, depending on the location of the different heat sinks and sources.

This thesis focuses on heat pumps used for heating, but with a slight modification: the high-temperature-side heat flows (Q_H from the heat source, and the Q_H portion of the heat to the building) are separated from the low-temperature-side heat flows (Q_L from ambient, and the Q_L portion of the heat to the building) in either time or space, as discussed in Section 2.3.



Figure 2.1: Temperature levels and energy flows for an absorption heat pump used for (a) heating, and (b) cooling.

2.1.2 Absorption heat pump working fluids

There are two working fluids in an absorption heat pump: the refrigerant and the absorbent. The refrigerant serves the same function in an absorption heat pump as it does in a vapor compression heat pump. It is a substance that undergoes a reversible phase change between liquid and vapor. The work in this thesis uses water as the refrigerant. In place of the compressor in a vapor-compression heat pump, an absorption heat pump uses a solution that absorbs the refrigerant (hence the name 'absorption' heat pumps). The absorbent has a high affinity for the refrigerant. In this thesis, the absorbent is an aqueous salt solution. The terms absorbent, absorbent solution, and salt solution are used synonymously throughout this thesis. Note also the commonly used term liquid desiccant, which is simply a type of absorbent solution where water is the refrigerant.

The two most commonly used absorbent-refrigerant pairs are lithium bromide / water (LiBr-H₂O) and water / ammonia (H₂O-NH₃). Although water is used in both systems, it is used for different purposes. In the LiBr-H₂O cycle, water is the refrigerant and LiBr salt the absorbent. The system pressure is near vacuum. Other salts can replace LiBr, such as those shown in Table 2.1, but systems using LiBr are the most developed. The other developed technology uses ammonia as the refrigerant and water as the absorbent. These systems operate near 5 atm. Using ammonia as the refrigerant enables temperatures for cooling applications below 0° C.

Mixtures of the salts in Table 2.1 are also possible. Iyoki and Uemura [4] compared several mixtures, including LiBr-LiCl, LiBr-ZnCl₂, CaCl₂-LiCl-ZnCl₂, and LiBr-ZnCl₂-CaBr₂. They performed simulations of heat pumps using each of these mixtures, and found the efficiencies to be within 20%, with some performing better at higher temperatures and some better at lower temperatures. Park et al. [5] later investigated adding calcium nitrate (Ca(NO₃)₂)

to LiBr, which they found to lower the solubility temperature. However, both of these absorbents are relatively expensive. Hassan and Hassan [6] suggested mixing the less expensive $CaCl_2$ with $Ca(NO_3)_2$, which they proposed for an open system liquid desiccant dehumidifier. They proposed a mixture of 50% $CaCl_2$ and 20% $Ca(NO_3)_2$, by weight, which they found to reduce the vapor pressure below that of pure $CaCl_2$. However, this did not lower the vapor pressure more than systems using a mixture of LiCl and $CaCl_2$ [7-10]. These absorbent mixtures are investigated with a thermodynamic model, as described in Chapter 3.

Absorbents	Symbol
Calcium chloride	$CaCl_2$
Lithium chloride	LiCl
Lithium bromide	LiBr
Calcium bromide	CaBr ₂
Calcium nitrate	$Ca(NO_3)_2$
Magnesium chloride	MgCl ₂
Zinc chloride	$ZnCl_2$
Water	H2O
Refrigerants	
Water	H ₂ O
Ammonia	NH ₃
Methanol	CH ₃ OH

Table 2.1: List of common absorbents and refrigerants for heat pumps and open-system liquid desiccant cooling systems.

2.1.3 Absorption heat pump cycle

Herold et al. [11] explain how an absorption heat pump cycle can be thought of as a combination of two rankine cycles: a power cycle and a heat pump cycle. A vapor-compression system uses a heat pump cycle, but it also uses a power cycle at the thermally-driven power plant that supplies the electricity to the compressor. An absorption heat pump is simply the

combination of these two cycles into one. The generator and absorber (discussed below) are analogous to the boiler and condenser at the power plant. And the evaporator and condenser of an absorption heat pump are the same as in a vapor compression heat pump.

The basic absorption heat pump cycle, shown in Figure 2.2, consists of four heat and mass exchange vessels, a pump, and two throttling valves. Although the process is continuous, it can be thought of as two independent steps: a desorption, or concentration, step, and an absorption, or diluting, step.

In the desorption step, high-temperature heat (Q_H from Figure 2.1) is supplied to a vessel of the absorbent salt solution (the generator). This heat, which could be from fuel combustion, waste heat, or solar thermal energy, evaporates some of the water (the refrigerant) which then travels out of the generator and into a second heat exchange vessel (the condenser). The water condenses there and releases heat to a heat sink (a portion of Q_I in Figure 2.1). This removal of water concentrates the salt solution; it becomes 'strong' in absorbent and 'weak' in refrigerant. Note that some authors refer to this concentrated solution as 'strong' and some authors as 'weak.' In this thesis, we use the terms concentrated and diluted to avoid confusion.

Between the desorption and absorption steps, the concentrated solution from the generator and the liquid water from the condenser move through expansion valves, reducing their pressures, to the absorber and evaporator, respectively. In the system using a membrane heat pump, there is no throttling valve because the whole system is at ambient pressure.

The absorption step is driven by the difference in water activities between the concentrated solution in the absorber and the pure water in the evaporator. Water evaporates from the pure water and condenses into the absorbent solution, increasing the temperature of the absorbent solution, and decreasing the temperature of the pure water until their vapor pressures
equalize. The difference between the absorber and the evaporator temperatures is the temperature lift discussed in Chapter 1. To continue the process, heat is removed from the absorber (part of Q_I) as heat is added to the evaporator (Q_L).

To complete the cycle, the diluted solution is pumped back to the generator. Often, an intermediate heat exchanger is placed between the generator and absorber to move heat from the hot, concentrated solution to the returning, diluted solution. This isolates the generator and absorber thermally and improves efficiency.



Figure 2.2: Type-I absorption heat pump schematic. HX = heat exchanger.

There are many variations of the simple design in Figure 2.2, including multi-stage and multi-effect designs [11, 12]. There is also a separate configuration called a type-II heat pump or

heat transformer (Figure 2.3). This operates differently than a type-I heat pump; it requires heat at the two intermediate temperatures and discharges heat at the two extremes. This can be used for industrial waste heat recovery, by upgrading unusable heat to a higher temperature [12]. A membrane heat pump, which is simply a combined evaporator-absorber component, can be used in a heat transformer, but the focus of this chapter is on a type-I heat pump, the type used for thermal energy storage and transport. Modifications required for energy storage and transport are discussed in Section 2.3.2.



-1/T

Figure 2.3: Type-II absorption heat pump (heat transformer). HX = heat exchanger.

2.2 Membrane processes

This section briefly discusses membrane processes, with a focus on membrane distillation, a thermally-driven membrane process similar to a membrane heat pump. It then discusses the use of membranes in absorption heat pumps and related technologies.

Artificial membranes are typically used to provide an efficient, cost-effective, and low energy way to separate and purify gases, liquids, and mixed phases. These separations are driven by chemical potential gradients, which can be from differences in concentration (diffusion), total pressure (reverse osmosis), electric potential (electrodialysis), and temperature (membrane distillation). Processes driven by temperature gradients, or thermally-driven processes, usually involve a phase change from liquid to vapor. Processes driven solely by thermodiffusion (or thermo-osmosis) are also possible [13], but not relevant here. The most common thermallydriven membrane process, and the one discussed here, is membrane distillation.

2.2.1 Membrane distillation

Membrane distillation is a separation method where a non-wetting, macroporous membrane is used with a liquid feed phase on one side of the membrane and a condensing, permeate phase on the other. It has been reviewed by several authors [14-19]. Just like the heat pump, the hydrophobicity of the membrane prevents liquid water from entering the pores, but allows water vapor to pass. The vapor pressure gradient created across the membrane by heating the feed liquid causes water to evaporate from the feed side and condense into the cooler permeate side. As evaporation cools the feed solution, heating is required to maintain vapor flux. The availability of low-cost thermal energy (e.g., waste heat or solar collected heat) makes membrane distillation a promising low-cost desalination option [20]. A similar thermally-driven membrane process is pervaporation [21], but pervaporation relies on a more complex membrane

to aid in separating species whose relative volatilities are quite close. Here the focus is on membrane distillation.

There are four main membrane distillation configurations: direct-contact, air-gap, vacuum, and sweep-gas [14, 18]. Direct contact and air gap membrane distillation are more relevant here as these are similar to the membrane heat pump: a vapor evaporates from a liquid, diffuses across a membrane, and condenses into a second liquid. The driving force is a vapor-pressure gradient. In air-gap membrane distillation, an air gap separates the membrane from the condensate stream, reducing sensible heat transfer.

The two design objectives in the heat pump and membrane distillation are the same, but the emphasis different. Both processes aim to maximize the overall vapor flux (the latent energy transfer) and to maximize the ratio of the latent to sensible energy transfers. In the heat pump, the emphasis is on the ratio of latent to sensible heat transfers, while the emphasis in membrane distillation is on a high flux. The operation of the two processes also differs. The membrane heat pump creates temperature differences from two pre-separated flows. Membrane distillation creates a species separation from two flows at different temperatures.

Several important insights of membrane distillation researchers are relevant to this thesis. However, instead of listing them here, they are discussed throughout the following chapters, where applicable.

2.2.2 Membranes in absorption heat pumps and related technologies

Research on membranes in heating, ventilation, and air conditioning (HVAC) applications in buildings have become more prominent in the last few decades. This section reviews the use of membranes in the following HVAC components: energy-recovery ventilators, evaporative coolers, dehumidifiers, air conditioners, liquid-desiccant regenerators, and absorption heat pumps.

Energy recovery ventilators (ERVs) exchanger heat and moisture between the outgoing, building exhaust air and the incoming, ventilation air from outside the building. Heat exchangers can recover the sensible portion of the energy, but not the latent energy (moisture). Using a membrane to separate the ventilation and exhaust airstreams enables both latent and sensible energy recovery. The heat and mass transfer humidifies and heats the ventilation air in the winter and dehumidifies and cools it in the summer. Several authors have investigated membrane-based ERVs [22-24] and some companies now have commercial products. They compete against other designs for ERVs, such as desiccant wheels [25].

Evaporative coolers, which cool the air in buildings, have also been investigated [26, 27]. They use a membrane to contain a thin-film of water next to an airstream. The air becomes humidified and cooled as water evaporates into the air. Since the air is also humidified, these evaporative coolers work only in dry climates. One issue with these systems is scale build-up and fouling on the membrane surface where the water is evaporating [27].

Dehumidifiers [28-31] use a membrane-contained thin film of liquid desiccant for removing moisture from buildings. Fouling is less of an issue here since mass transfer is into the liquid, diluting the solution near the membrane surface. Membrane dehumidifiers are used in industrial processes, but they have not been investigated for buildings until more recently.

A membrane air conditioner [32-35] provides both cooling and dehumidification, usually with a liquid desiccant. These liquid-desiccant air conditioning systems can use membranes to control flow and contain the desiccant from entraining into the air [35]. The design by Kozubal et al. [34] integrates a membrane evaporative cooler and a membrane dehumidifier into one unit.

Its advantage is that it does not require any supplemental cooling from a vapor-compression unit or cooling towers. Section 2.3.2 discusses these air conditioners in more detail as they relate to energy storage and transport.

Liquid-desiccant regenerators re-concentrate, or regenerate, the liquid desiccant used in membrane dehumidifiers and air conditioners back to its original concentration. Several authors have proposed using membrane processes for regeneration: Wang et al. [36] proposed using vacuum membrane distillation, Li and Zhang [37] proposed using electrodialysis, and Al-Farayedhi et al. [38] and Al-Sulaiman et al. [39] proposed using reverse osmosis. All of these, though, regenerate the solution with energy that ultimately comes from electricity, negating the benefits of thermally-driven cooling. Thermally-driven membrane distillation will also work for this regeneration, with some of these methods discussed in Section 2.3.

Absorption heat pumps can also benefit from the use of membranes. These are closed systems operating at a pressure far from ambient, as opposed to the open, ambient pressure systems discussed above. Using membranes in absorption heat pumps has been discussed primarily to enhance the heat and mass transfer and thus reduce their size and cost. Drost et al. [1, 2] from the Pacific Northwest National Laboratory (PNNL) recently summarized their work on making absorption heat pumps more compact by using membranes that offer 'mechanically-constrained ultra thin films' of the absorbent and refrigerant. The reduced thickness lowers the heat and mass transfer resistance and reduces size. Separately, Schaal et al. [3] from Universität Stuttgart worked on a similar project, focusing on using membranes to reduce size and cost, and also to reduce sensitivity to vibration to enable absorption heat pumps for mobile applications. In 2008, the Fraunhofer Institute for Environmental, Safety, and Energy Technology started a comprehensive project to design compact absorbers using membranes [40-42].

Smaller projects have also investigated heat pump components in isolation. In 2004, Riffat et al. [43] proposed and analyzed pervaporation for regeneration with a membrane between the generator and condenser. Similarly, Thorud et al. [44] experimentally investigated the use of a membrane-contained absorbent in the generator, but they use microporous membranes (membrane distillation) instead of the dense membranes used in pervaporation. This is essentially absorbent regeneration using vacuum membrane distillation. Kim et al. [45] investigated the same concept except their focus was on very small systems for electronics cooling. Researchers have also investigated the use of membranes in the absorber component. Chen et al. [46] investigated the use of hollow-fiber membranes and non-porous hollow fibers in the absorber. The porous hollow fibers allow transfer of vapor from the evaporator, while the non-porous fibers act as a heat exchanger with ambient to keep the absorber temperature low when it is used in a heat pump for cooling.

All of these projects focus on reducing the size, and potentially cost, of the four heat pump components: the generator, condenser, evaporator, and absorber. The purpose of the membrane heat pump proposed here is to enable ambient pressure operation. This will not necessarily reduce the size of the four heat pump components as the above designs. But it can make their construction much lighter and simpler by reducing the pressure difference they must maintain with ambient. Ambient pressure operation also has advantages for absorption heat pumps used for storing and transporting thermal energy, as discussed in the next section.

2.3 Thermal energy storage and transport

The membrane heat pump in this thesis operates at ambient pressure, which differentiates it from the absorption heat pumps using membranes discussed above. The eventual goal of this

research is to provide an efficient way to store thermal energy for long periods and to transport thermal energy over long distances.

Thermal energy storage is conventionally done in heated water tanks. These tanks work well for short-term storage, such as hot-water heaters, but they cannot store thermal energy efficiently for longer periods because there are inevitable losses to the ambient, even with insulation. Storing a heat pump's concentrated absorbent can be done at ambient temperature, eliminating losses. A working group from the International Energy Agency (IEA) investigated this in a project titled "Advanced storage concepts for solar houses and low energy buildings" [47], which ran from 2003 to 2007. This working group researched new ways to store heat in systems providing heating or cooling to buildings.

Heated water is also the standard fluid for thermal energy transport. This works well for short distances, but thermal losses are even more important here because pipes have a higher surface area to volume ratio than tanks. Similar to longer-term storage, pumping a heat pump's absorbent long distances at ambient temperature would eliminate thermal losses. A second working group began a project in 2006 titled "Transportation of Thermal Energy Utilizing Thermal Energy Storage Technology" [48, 49]. This working group focused on ways to use thermal energy at user sites located more than 10 km from a site with excess thermal energy (e.g., a power plant).

These IEA working groups focused on using the absorbent to store and transport thermal energy. As mentioned, this has the advantage of operating at ambient temperature, which limits thermal losses. However, it is costly to store this absorbent in large, pressurized tanks (or depressurized tanks in the case of LiBr). And pumping at the required high or low pressures means the pipes are more expensive and there is an increased potential for leaks. This latter

problem is important considering the pumped fluid is either ammonia, which is toxic, or LiBr, which is highly corrosive. Operating an absorption heat pump at ambient pressure enables storage in a much less expensive, unpressurized tank and pumping in much less expensive, plastic tubing with a lower risk of leaks.

The following two sections clarify the work done by the two IEA working groups, which show how an ambient-pressure heat pump would be valuable. The IEA working groups focused on the same topics for both thermal energy storage and transport: phase change materials and the absorbent in an absorption heat pump.

2.3.1 Storage and transport in a phase change material (PCM)

Phase change materials (PCMs) absorb and release heat as they switch between the solid and liquid states. Their energy density is larger than sensible storage and they can also absorb and release heat at a constant temperature. Their higher cost is a key disadvantage, although some are cheaper than others. For example, ice storage is a low-cost option with much interest recently [50-54]. Ice storage, though, cannot be used for heat storage and like all other solidbased storages is not ideal for transport.

PCMs have low thermal conductivity. They solidify first around the edges and then the low conductivity of the solid slows further solidification near the center. Encapsulating the PCM in smaller vessels eases this problem, but also increases cost. The problem of low conductivity applies to most solid materials, including the adsorption and chemical heat pumps discussed below. There are modifications to overcome the problem of low thermal conductivity. For more details on PCMs for heat storage, refer to any number of review articles [55-62].

Transport of thermal energy using PCMs is more difficult, but there are researchers looking at transporting PCM either by rail or truck [63], or by suspensions of PCM in a pumpable slurry [64].

2.3.2 Storage and transport in a heat pump's absorbent solution

Absorption heat pumps, as well as adsorption and chemical heat pumps, can be modified to store or transport thermal energy. In each case, the storage and transport is done a little differently, but the focus here is on absorption heat pumps which are the most developed technology to date [47, 63]. Adsorption and chemical heat pumps are discussed briefly at the end of this section.

The absorbent in the absorption heat pump is what enables energy storage or transport. Research thus far has focused on systems operating either at very high pressures (NH_3 - H_2O) or at vacuum pressure (LiCl, LiBr). So while no thermal insulation is needed for the pipes or tanks, they must be constructed to withstand the large pressure difference with the atmosphere. This requires higher upfront costs and has a greater potential for leaks. There are some advantages and disadvantages to choosing the working fluid, and it also depends on whether it is used for thermal energy storage, thermal energy transport, or both.

For thermal energy storage, the operation of the generator and condenser are separated, in time, from the absorber and the evaporator (Figure 2.4). The generator stores the concentrated absorbent solution, which is at room temperature and thus there are no thermal losses. When heat is needed, a valve releases the solution into the absorber where it absorbs the refrigerant. This releases heat and increases the solution's temperature.



Figure 2.4: Absorption heat pump system designed for energy storage or transport. Evaporator and absorber are separated from condenser and generator, either in space or time. The membrane heat pump is an evaporator-absorber component.

Several researchers have looked at storing this absorbent solution for cooling buildings, although in this field it is usually referred to as a liquid desiccant. Using thermal energy to concentrate the liquid desiccant alleviates the peak electricity demand of summer air conditioning. The ability to store the desiccant is also attractive for systems using solar-thermal collectors, where solar radiation and the requirement for cooling do not always coincide. Researchers have investigated both closed systems [65-70] and open systems [71-74]. The closed systems are similar to conventional LiBr absorption heat pumps, operated under vacuum, but the absorbent is usually LiCl. The approach by Bales [69] includes not only storage in the

concentrated absorbent but also in the solid hydrate, which absorbs even more energy when it solidifies. As it goes back into solution, energy is released. This secondary storage mechanism increases the energy density of the storage. This concept has been commercialized by ClimateWell AB in Sweden.

The open systems are of interest here, as they have several advantages in both energy savings and humidity control. In these systems, the desiccant is in direct contact with the air, providing dehumidification [75, 76]. These systems have been commercialized by companies such as PAX Streamline and Kathabar for dehumidifying ventilation air in supermarkets, where humidity control is important. They can also supplement the sensible cooling done by low-energy direct or indirect evaporative coolers with independent humidity control, as in [29, 77].

A technology developed at the National Renewable Energy Lab integrates indirect evaporative cooling and desiccant drying in a single device, which can independently cool and dehumidify the air for comfort conditioning of buildings [34, 78]. Like the absorption heat pump discussed in this thesis, this device also uses microporous membranes. There are several advantages of liquid-desiccant air conditioning over vapor-compression air conditioning, as discussed elsewhere [34, 75, 76]. Also, the open system has advantages over the conventional, closed system by storing the absorbent solution at ambient pressure in an unpressurized tank. But these open systems do not provide heating. Adding a membrane heat pump, which also operates at ambient pressure, can provide this heating.

For energy transport, the absorbent solution can be pumped from a location with excess heat (the source site) to a location needing heat (the user site). The modification required for transport is to separate, in space, the generator and condenser from the evaporator and absorber (Figure 2.4). At the source, heat is added to the generator, concentrating the absorbent solution

with the evaporated vapor condensing into the condenser. A pump then pushes the absorbent solution through a pipe to the user site, where it absorbs vapor in the absorber and increases its temperature.

Transporting thermal energy in the absorbent solution was proposed by Kashiwagi, et al. [79] while Kang et al. [80] modeled and analyzed the systems in more detail. Kang et al. discuss several advantages over water-transport systems. No insulation is required on the pipes since the absorbent solution is pumped at ambient temperature. The pipes are also smaller because of the higher energy density of the absorbent solution. These both reduce cost and complexity of the piping system so that energy can be transported over further distances. The large, centralized generator-condenser component would also likely be less expensive than many small ones built at each user site. The generator-condenser component could be at a waste-heat source or at a central solar-thermal plant. A small absorber-evaporator component is at each user site. Recall that the membrane heat pump discussed in this thesis is an absorber-evaporator component.

Kang et al. [80] also mention several disadvantages of their proposed system, some of which are specific to the chosen absorbent. They consider both LiBr-H₂O and H₂O-NH₃ systems. LiBr is more expensive than ammonia and is also corrosive. Ammonia, on the other hand, is toxic and also is transported as both pure liquid and a water-ammonia mixture, requiring twice as much pipe and more energy.

Conventional absorption heat pumps use a liquid absorbent and a refrigerant. These actually belong to a broader category of thermally-driven heat pumps called sorption heat pumps. Instead of an absorbent, the sorbent can be a solid adsorbent bed (adsorption heat pumps) or a solid-gas reactor (chemical heat pumps). Adsorption heat pumps use solid adsorbents with a high

affinity for a refrigerant, usually water. Chemical heat pumps use a chemical reaction, such as methanol decomposition and synthesis [63].

Using adsorbents or chemically reacting species in place of the liquid absorbent requires a few modifications. Adsorption heat pumps can use either physical or chemical adsorbents, but physical adsorbents are preferred for low-temperature applications (e.g., solar-thermal collectors) [81]. Common physical adsorbents for adsorption heat pumps are silica gel, zeolite, and activated carbon. Refrigerants are usually water, ammonia, or methanol, although others exist. Several researchers have looked at adsorption heat pumps for energy storage [82-86] and for energy transport [63, 87, 88], as well as chemical heat pumps for energy storage [89-91] and for energy transport [92, 93]. One major disadvantage of these systems is that the transported fluid is a gas rather than a liquid. This requires larger diameter pipes to limit pressure drop. The second disadvantage is that the sorbent is solid, which as discussed in the section on PCM, is limited by its low thermal conductivity.

The membrane heat pump proposed here offers many of the advantages of the absorption heat pumps above. In addition, the system here operates at ambient pressure. This enables simpler and smaller components such as valves, pumps, pipes, and tanks. In particular, the unpressurized tanks storing the absorbent can be much larger for the same cost as a pressurized tank for a conventional system. It is also an open system with more possibilities for efficient cooling technologies. Finally, with water as the refrigerant, the absorbent is the only fluid pumped from one site to the other, as opposed to pumping both pure ammonia and an ammoniawater solution as in the systems discussed above. The next chapter focuses on designing a membrane heat pump that can be used in these energy storage and transport systems.

CHAPTER 3 Theory and design

This chapter brings together the relevant theory and design principles from the fields of membrane technology, absorption heat pumps, and heat exchangers. A theory on absorption heat pumps operating at ambient temperature has not been developed prior to this thesis. For any absorption heat pump, a benchmark is the maximum, theoretical temperature lift, which is discussed in Section 3.1. The membrane heat pump will not reach this maximum due to sensible heat transfer from the heated absorbent solution to the cooled, evaporating refrigerant. The goal of the heat pump design is to come as close as possible to this maximum temperature lift.

Theory on absorption heat pumps at ambient pressure has yet to be developed. After discussing the standard theoretical benchmark, this chapter develops this new theory by deconstructing the governing equations of the membrane heat pump process to determine the key design and operating parameters controlling the temperature lift. Then, with several assumptions, it presents a new analytical solution of the temperature lift. This shows explicitly how the key design and operating parameters influence the temperature lift. In the next chapter, a finite difference model calculates the temperature lift after relaxing many of the assumptions of the analytical solution. The results from these three methods for calculating the temperature lift (the theoretical maximum, the analytical solution, and the numerical model) are compared in Chapter 5.

3.1 Theoretical-maximum temperature lift

The maximum possible temperature lift can be estimated with a few simple equations. It is simply the difference between the solution and water temperatures when both liquids have reached equilibrium with the same water activity, or vapor pressure. This maximum temperature lift is then a benchmark to compare actual temperature lifts to, whether they are modeled or measured experimentally.

Using the Clausius-Clapeyron equation, the vapor pressures above two liquids are related with:

$$\ln\left(\frac{p_{\nu,1}}{p_{\nu,2}}\right) = \frac{\Delta H_{\nu a p}}{\left(R/M\right)} \left[\frac{1}{T_1} + \frac{1}{T_2}\right]$$
(3.1)

where R is the universal gas constant, M the molecular mass (in this case water), ΔH_{vap} the enthalpy of vaporization of water, T temperature, and p_v vapor pressure. Letting condition 1 represent water and condition 2 represent the absorbent solution, the above equation becomes:

$$\ln\left(\frac{p_{v,w}}{a_s p_{v,w}}\right) = \frac{\Delta H_{vap}}{\left(R/M\right)} \left[\frac{1}{T_w} + \frac{1}{T_s}\right]$$
(3.2)

where a_s is the water activity of the ideal-gas mixture above the absorbent solution. Rearranging, and using the definition of the temperature lift gives:

$$\Delta T_{\text{lift,max}} = \left[\frac{1}{T_w} + \frac{\left(R/M\right)}{\Delta H_{vap}} \ln a_s\right]^{-1} - T_w$$
(3.3)

This equation is the theoretical maximum temperature lift based on thermodynamic equilibrium. It shows the importance of choosing the working fluids. The water activity of the absorbent should be minimized while the enthalpy of vaporization of the refrigerant should be maximized. There are, of course, many other considerations. For example, water is a practical choice for the refrigerant since it is non-toxic and has a negligible cost. The selection of the absorbent is discussed in Section 3.2.1

Eq. (3.3) also shows that the maximum temperature lift is a function of the inlet water temperature: higher inlet temperatures result in higher temperature lifts. The effect, though, is

small. The difference between the maximum temperature lifts at 20 and 60° C inlet temperatures and high concentrations is 8%. But the inlet temperatures have a separate effect on the actual temperature lifts, as discussed in Section 5.3.

3.2 **Designing a membrane heat pump**

3.2.1 Selecting and characterizing the absorbent

Selecting the absorbent properties for a membrane heat pump is based on the same criteria as that for a conventional absorption heat pump, plus some additional constraints. The model requires each of the absorbent properties in Table 3.1. These can be estimated with thermodynamic models or by measuring them experimentally. Experimental data is preferred, but not available for all possible mixtures. For pure LiCl and CaCl₂, which are used in the experiments, empirical data-regression correlations from Conde [94] are used. For mixtures, the electrolyte software from OLI Systems, the OLI Stream Analyzer, calculates these properties for different mixtures of salts based on theory and data regression techniques. This thesis considers the salts CaCl₂, CaBr₂, LiCl, MgCl₂, and the mixtures of these salts.

Absorbent property	Symbol	Units
water activity (vapor pressure reduction)	a_{w}	-
viscosity	μ	kg/m-s
thermal conductivity	λ	W/m-K
specific heat capacity	c _p	J/kg-K
differential heat of dilution (heat of mixing)	ΔH_{mix}	J/kg
solutal diffusivity	D ₁₂	m^2/s
surface tension	γ	N/m
solubility limit	T _{sat}	С
density	ρ	kg/m ³

Table 3.1: Absorbent properties needed for modeling

The ultimate goal in selecting the absorbent is to optimize it based on the above properties and cost. However, the optimal absorbent depends on the application. For storage applications, the unit cost (\$/kg) of the absorbent is key, as lowering this cost enables higherenergy storages. It is also desirable for the heat pump to work over a large range of inlet concentrations, allowing a large swing in the storage concentration, and increasing energy storage density. Even after these considerations, there are still others that are specific to each application. How much absorbent is stored? What are the required temperature lift and the available heat source temperature? For transport applications, it also depends on the distance between the source site and the user site. The approach here is to look at these tradeoffs in general to help frame future optimization problems looking at a specific application. In particular, this study looks at four properties: water activity, saturation mass fraction, cost, and viscosity.

The temperature lift is a strong function of the absorbent's water activity, which increases with higher mass fractions. The mass fractions are limited, though, by saturation. The saturated mass fraction depends on temperature, and is therefore set by the minimum operating temperature anywhere (e.g., tanks and pipes) in the system. The system should always operate below the saturation mass fraction. Once the minimum operating temperature is known, the maximum mass fraction can be set, which gives the water activity. Costs for different absorbents vary widely (e.g., costs of LiCl are 10-20 times higher than CaCl₂). Thus, the analysis searches for mixtures that substitute lower-cost salts for higher-cost salts, without degrading performance. Finally, viscosity is important for thermal energy transport over long distances, and in a similar way, the analysis searches for low-cost substitutes that lower viscosity without degrading performance.

3.2.2 Selecting and characterizing the device geometry

A membrane heat pump device brings absorbent solution and water together in a way that maximizes the temperature lift. Membranes provide inherently large surface area per unit volume. As discussed in the Introduction, the 'membrane' used here is actually two membranes with an air gap in between. An air gap has a higher resistance to heat transfer than a membrane, but a lower resistance to mass transfer. Thus, using an air gap increases the ratio of latent to sensible energy transfer. Before analyzing the appropriate air gap widths, three general features of a heat pump design must be chosen: flow directions, membrane type, and module layout.

The two flows in the membrane heat pump can be parallel flow, counter-flow, or crossflow. A counter-flow heat exchanger maximizes the log-mean temperature difference and therefore minimizes the required surface area. However, a heat exchanger in counter-flow means the exit for the first fluid is on the same side as the entrance for the other, and thus manifolding these flows is difficult. For this reason, many heat exchangers are built in cross-flow. For a membrane heat pump, like a heat exchanger, a counter-flow arrangement theoretically gives the best performance. However, it is not just the difficulty of physically manifolding the absorbent and refrigerant flows that is important. Since the exit of the heated solution coincides with the entrance of the cooler water, the design must limit their thermal interaction. In other words, in a counter-flow arrangement, it is possible that much of the heat gained by the solution will be lost back to the water at the exit header. This inherent heat loss strongly favors a cross-flow design for a membrane heat pump.

Regardless of the flow directions chosen, the design can use two types of membranes: flat-sheet membranes or hollow-fiber membranes. Flat sheet membranes, as the name suggests, are thin, flexible semi-permeable sheets. To be used in the heat pump, they would require a

support for the air gap. This could be a rigid, corrugated spacer or a flexible support with a honey-comb structure (Figure 3.1a and b). The support reduces the temperature lift since it limits the area available for mass transfer and increases the sensible energy transfer with conductive shorts across the air gap. Ideally, these supports would be made from low-conductivity plastics such as polystyrene to limit these conductive shorts. Hollow fibers do not require air-gap supports since they are self supporting. This is easiest to think about by considering two hollow fiber membranes, as shown in Figure 3.1c. The water flows through one fiber while the solution flows through the other. The space between the fibers acts as the air gap.



(a)



(b)



Figure 3.1: Spacer designs to support the membranes around the air gap: (a) perforated, corrugated spacer, (b) honeycomb spacer, (c) integrated hollow fiber spacer using cylindrical walls for support.

The selection of the type of membrane module depends on the type of membrane. The three most common membrane module arrangements are the spiral-wound module, the plateand-frame module, and the shell-and-tube module. The spiral-wound and plate-and-frame modules use flat sheets while the two variations of the shell-and-tube module use hollow fibers. The following paragraphs assess these modules for their potential use as a membrane heat pump.

Reverse osmosis uses spiral-wound modules. Since this is a large membrane market, spiral-wound modules are appealing. However, spiral wound modules have only one inlet and two exits (Figure 3.2), which is not suitable for the heat pump. The fluid inlets and outlets are also, in general, very close together, leading to undesirable heat exchange between the two fluids outside the membrane area. The plate-and-frame module (Figure 3.3) does not have these limitations. Its major advantage is its simple geometry. But both the spiral-wound and plate-and-frame modules have a major disadvantage: they require a performance-degrading spacer in the air gap.



Figure 3.2: Spiral-wound module using flat sheets. Single inlet ('Feed inlet') makes this module unsuitable for the membrane heat pump.



Figure 3.3: Plate-and-frame module using flat sheets in a counter-flow arrangement.

The appeal of modules with hollow fibers is that the hollow fibers are self supporting. But the conventional shell-and-tube module (Figure 3.4) does not lend itself to an air gap with commercially-available modules. An air gap is possible if a hollow-fiber membrane with an integrated gap could be used, such as those proposed by Li et al. [95]. A schematic of these annulus membranes is shown in the detail in Figure 3.4. The gap space in these membranes is only 5 μ m though, which is too small for the heat pump application, as shown in Chapter 5. The module in Figure 3.5 is another option using hollow fibers. It consists of an interspersed bundle of two sets of hollow-fiber membranes. Each set of fibers is manifolded together at the inlets and outlets. This type of module was proposed for two separate applications. Majumdar et al. [96, 97] proposed using this module as a hollow-fiber contained liquid membrane. The interstitial space is filled with a liquid that enhances the transport of one species with a suitable carrier species, leading to improved separation (see [98]). In the second application, discussed by Sidhoum et al. [99] and Liu et al. [100], the interstitial space is used as an intermediate pressure permeate, received from the feed through one set of fibers. The other set of fibers is a second, lower-pressure permeate. This allows staging internal to the module. For a heat pump module, the design in Figure 3.5 can be used with the two sets of fibers containing either solution or water and with the shell filled with air. However, this design was not selected here due to the uncertain geometry of the air gap: the model cannot easily incorporate the complex geometry of the air gap for model-experiment validation.

This research uses a new module with two sets of hollow-fiber membranes. It consists of alternating rows of hollow fibers, with the air-filled shell between the rows acting as the air gap (Figure 3.6). As discussed before, cross-flow is used to simplify the collection of the refrigerant

and absorbent and to reduce the sensible heat transfer between these fluids outside the masstransfer area.



Figure 3.4:.Conventional shell-and-tube module using hollow-fiber membranes. One fluid flows through the inside of the fibers (the lumens) while the other flows around fibers (the shell). Annulus design, with an integrated air gap inside a hollow fiber membrane, is from Li et al. [95].



Cross section view

Figure 3.5: Internally-staged permeator with two sets of hollow fiber membranes. Conventionally used with shell side as an intermediate pressure stage, but the shell side could act as the air gap in the heat pump. But this uncertain air gap geometry is not appropriate for model validation though.



(a)





Figure 3.6: New, cross-flow hollow-fiber module used for the prototypes. (a) Top view schematic. (b) Picture of prototype module from AMT. (c) Detail model of hollow-fibers at headers (corner). Ends of fibers are potted into the headers such that liquids flow into fiber lumens, but not into the shell.

This module (Figure 3.6) is used for the experimental prototype. The prototype was custom built by Applied Membrane Technology, Inc. (AMT) to the specifications listed in Table 3.2. This manufacturer has experience with two polypropylene hollow fiber membranes: the Oxyphan[®] and Accurel[®] PP membranes, both manufactured by Membrana. For this reason, these two membranes were considered for this design. The parameters characterizing these membranes are listed in Table 3.2 and Table 3.3, with methods for estimating these parameters discussed in the next section.

The Accurel membranes are more porous and have a higher permeability than the Oxyphan membranes. However, previous researchers found structural issues with modules built by AMT with the Accurel membranes. Some fibers broke during construction [101] and some pores became wetted with epoxy during potting with subsequent water leakage through these pores [102]. Due to these reasons, as well as recommendations from AMT, the first-generation prototype ('hollow fiber v.1') was built with the Oxyphan fibers. Note, though, that some

modules using the Accurel fibers were without problems [102], and modules using these fibers ('hollow fiber v.2') are considered in the modeling of the 'second-generation' prototype in the following chapters. This prototype has not yet been built. These two prototype modules are modeled in the next Chapter, along with two other hypothetical modules using flat sheets: one with an air gap, and one without (Table 3.4).

Table 3.2: Cross-flow hollow-fiber module specifications (prototypes from AMT). Membrane porosity, tortuosity factor, and pore size were determined with the experimental techniques described in the text.

Module dimensions	
length, L^1 (mm)	150
width, W^1 (mm)	150
number of rows, N _{rows}	12
fibers per row, N _{fibers}	300
air-gap width, d _{gap} (mm)	
Prototype #1	0.56
Prototype #2	0.71
Prototype #3	0.91
Hollow-fiber membranes:	
type	Oxyphan-280
manufacturer	Membrana
outer diameter, d _o (mm)	0.38
outer diameter, d _o (mm) inner diameter, d _i (mm)	0.38 0.28
outer diameter, d_o (mm) inner diameter, d_i (mm) porosity, ϵ	0.38 0.28 0.43 ²
outer diameter, d_o (mm) inner diameter, d_i (mm) porosity, ε tortuosity factor, τ	0.38 0.28 0.43^{2} 5.6^{3}
outer diameter, d_o (mm) inner diameter, d_i (mm) porosity, ε tortuosity factor, τ mean pore diameter, d_p (µm)	$\begin{array}{c} 0.38\\ 0.28\\ 0.43^2\\ 5.6^3\\ 0.062^3\end{array}$
outer diameter, d_o (mm) inner diameter, d_i (mm) porosity, ε tortuosity factor, τ mean pore diameter, d_p (µm) N_2 permeance from [102] ⁴	$\begin{array}{c} 0.38\\ 0.28\\ 0.43^{2}\\ 5.6^{3}\\ 0.062^{3}\end{array}$
outer diameter, d_o (mm) inner diameter, d_i (mm) porosity, ε tortuosity factor, τ mean pore diameter, d_p (μ m) N ₂ permeance from [102] ⁴ (cm ³ /cm ² /s/cmHg)	$\begin{array}{c} 0.38\\ 0.28\\ 0.43^2\\ 5.6^3\\ 0.062^3\\ 0.0194\end{array}$
outer diameter, d_o (mm) inner diameter, d_i (mm) porosity, ε tortuosity factor, τ mean pore diameter, d_p (µm) N_2 permeance from [102] ⁴ (cm ³ /cm ² /s/cmHg) N_2 permeance from this study ⁵	$\begin{array}{c} 0.38\\ 0.28\\ 0.43^{2}\\ 5.6^{3}\\ 0.062^{3}\\ 0.0194\end{array}$

¹ length and width correspond to membrane area available for heat and mass transfer ² porosity measured with density measurements

³ mean pore diameter and tortuosity factor measured with gas-permeation method

 4 N₂ permeance from [102] average of five 450-fiber modules

 5 N₂ permeance average of two 120-fiber test modules (Figure 3.8)

Table 3.3: Cross-flow, hollow-fiber module specifications (hollow fiber v.2). No physical prototype, model only. Membrane porosity, tortuosity factor, and pore diameter from literature [101-104].

Module dimensions	
length, L (mm)	150
width, W (mm)	150
number of rows, N _{rows}	10
fibers per row, N _{fibers}	200
air-gap width, d_{gap} (mm)	1
Hollow-fiber membranes ¹ :	
type	Accurel PP
manufacturer	Membrana
outer diameter, d _o (mm)	0.63
inner diameter, d _i (mm)	0.33
porosity, ε	0.75
tortuosity factor, τ	2
mean pore diameter, $d_p(\mu m)$	0.2
N_2 permeance from $[101]^2$	
$(cm^3/cm^2/s/cmHg)$	0.175

¹ Membrane properties estimated from literature and manufacturer data. See text for details. ² N₂ permeance from [101] average of a 180-fiber module and a 268-fiber module

Module dimensions	no air gap	1-mm air gap
Number of channels	15	40
Length of channel (m)	0.5	0.5
Width of channel (m)	0.2	0.3
Height of channel (m)	0.001	0.001
Hypothetical membrane parameters		
Porosity, ε	0.7	
Pore diameter, $d_{pore}(\mu m)$	0.2	
Thickness, δ_{mem} (µm)	100	
Thermal conductivity, $\lambda_{polymer}$ (W m ⁻¹ K ⁻¹)	0.2	
Tortuosity factor, τ	2	

Table 3.4: Flat-sheet module specifications without and with an air gap. No physical prototype, model only.

3.2.3 Selecting and characterizing the membrane

Once selected, the membrane must be characterized to estimate its heat and mass transfer coefficients for use in the numerical model. The membrane parameters used in the model are the porosity, tortuosity factor, pore size, and thickness.

The porosity is a measure of the void space of the membrane; the ratio of open volume to the total volume. The tortuosity factor is more difficult to define. Theoretically, it is the square of the tortuosity, with the tortuosity defined as the ratio of the length of an actual pore to the straight-through thickness of the membrane. The tortuosity factor is a squared term because it accounts for both the actual additional pore length and the resulting increase in the actual molecule's velocity over the interstitial velocity [105]. A full derivation of this squared term can be found in Epstein [105]. The problem is that the tortuosity factor is often used as an adjustable parameter in membrane mass transfer modeling, and therefore takes into account many other factors, including pore shape [106], pore size distribution [107], pore connectivity [107, 108], and pore constrictedness [109]). Addressing all of these concerns is outside the scope of this thesis. Here the tortuosity factor uses a common correlation for the parametric analysis and is measured experimentally for the hollow fiber v.1 prototype modules.

The pore size, as the name implies, is the size of the membrane's pores. However, this is not as straightforward as it sounds. In reality, there is not a single pore size but a distribution of sizes. However, a membrane's pore-size distribution is usually not reported with pore size data and it is more difficult to measure than just a mean pore size. The flux through each pore depends on that pore's size, and with a distribution of pore sizes, the flux will be different through each pore. An extensive study on this issue, presented in Appendix A, looks at the effect

of pore-size distribution on the flux in a membrane heat pump, as well as on the related process of membrane distillation.

There are some constraints to remember for the membrane parameters. They are considered in the parametric analysis in Section 5.1.3. The tortuosity factor is rarely near 1; a value of 2 is common and a value of 1.5 better than average. The porosity obviously must be less than 1 and is normally less than 0.8. The pore size must be small enough so that the breakthrough pressure is not exceeded, which would cause liquid to leak into the gap. This analysis considers pore sizes up to 0.5 μ m. Since membranes have a pore size distribution, a membrane with a mean pore size of 0.5 μ m may have some pores near 1 or 2 μ m. Thus, a highest mean pore size of 0.2 may be more appropriate. The final parameter, the membrane thickness, must be large enough for structural support. Many membranes used for membrane distillation are near 100 μ m, with some as thin as 50 μ m. Also, it is possible to add a highly porous, large-pore-size support onto a thin layer with smaller pore sizes to prevent wetting.

The literature includes data on the Accurel PP membranes, including the nominal pore size from the manufacturer [110]. The porosity is reported to be between 0.6 and 0.8 in research by Sirkar et al. [101-104]. The tortuosity factor is more difficult to estimate. A commonly used equation for the tortuosity factor for phase-inversion membranes is [111]:

$$\tau = \frac{(2-\varepsilon)^2}{\varepsilon} \tag{3.4}$$

For the range of porosities above, this equation calculates tortuosity factors between 1.8 and 3.2. Modelers commonly assume a tortuosity factor of 2 for this type of membrane (e.g., see [14, 112-115]).

To add confidence to the estimates of the membrane parameters, the model-predicted membrane mass transfer coefficients are compared to experiments performed by Sirkar and Li [101-103]. Their study used Accurel hollow fibers in modules supplied by AMT for directcontact membrane distillation, with the feed flowing on the shell side and the permeate flowing through the lumens. With their heat and mass flux data, the membrane mass transfer coefficients are calculated for three of their modules using a log-mean vapor pressure difference and a calculated temperature polarization coefficient. A temperature polarization coefficient corrects the overall mass transfer coefficient to be based on the bulk vapor pressures instead of the vapor pressures at the liquid-membrane interfaces (see Section 4.2.8). The calculated membrane mass transport coefficients are 420, 440, and 520 (x 10^{-6} kg m⁻² s⁻¹ kPa⁻¹). Using the values listed in Table 3.3, the equations from Chapter 4 predict a membrane mass transfer coefficient of 440 (x 10^{-6} kg m⁻² s⁻¹ kPa⁻¹) at the operating temperatures and pressures from their study. Thus, the model-predicted value is within the experimental range, and is adequate for estimating temperature lifts in the heat pump model.

There are also membrane parameters for the Oxyphan fibers reported in the literature, but these values vary more than the Accurel fibers. Also, the manufacturer does not report the nominal pore size. For these reasons, the parameters are determined experimentally for the Oxyphan fibers. The pore structure of the Oxyphan membrane, after breaking the fiber in liquid nitrogen, is shown in the scanning electron microscope (SEM) image of Figure 3.7.



Figure 3.7: SEM image of cross section of Oxyphan hollow fiber after breaking the fiber in liquid nitrogen.

The porosity of the Oxyphan fibers was estimated using the so-called "pat-and-weigh technique." Seven samples were weighed with a Sartorius ME235 scale equipped with a polonium source to remove static charges. The porosity is calculated using [116]:

$$\varepsilon = 1 - \frac{\rho_{\text{membrane}}}{\rho_{\text{polymer}}}$$
(3.5)

where the density of the bulk membrane (ρ_{membrane}) is measured by weighing a fiber of known volume (inner and outer diameters measured from cross-section SEM images). The density of the polymer (polypropylene) is assumed to be 0.91 g/cm³ [117].

Gas permeation measurements [118, 119] are used to calculate the mean pore size and the porosity-tortuosity ratio. Nitrogen gas is supplied to the lumen side of a 20-cm long tubular module containing 120 fibers (Figure 3.8). The gas then flows into the lumens, across the membrane, and into the shell side of the module. A mass flow rate measurement and the membrane area are used to calculate the mass flux through the pores. This mass flux through the pores, normalized by the pressure difference across the membrane, is a combination of viscous and Knudsen flow, which for cylindrical coordinates is:

$$\frac{J_{\rm N2}}{\Delta p} = \frac{M_{\rm N2}}{RT} \frac{2}{d_{\rm o} \ln(d_{\rm o}/d_{\rm i})} \left[\frac{\varepsilon}{\tau} \frac{d_{\rm p}}{3} \sqrt{\frac{8RT}{\pi M_{\rm N2}} + \frac{\varepsilon}{\tau} \frac{d_{\rm p}^2}{32\mu}} \overline{p} \right]$$
(3.6)

where d_i and d_o are the inner and outer diameters of the fiber, M_{N2} and μ the molecular mass and viscosity of nitrogen gas, d_p the mean pore size, and \overline{p} the mean pressure in the pores. For details on combined viscous-Knudsen flow, see Section A.3.1 in Appendix A. The nitrogen mass flux has a linear relationship with the mean pressure, and can be rewritten with the slope and intercept renamed to two experimental parameters [118, 119]:

$$\frac{J_{N2}}{\Delta p} = B_0 + S_0 \overline{p} \tag{3.7}$$

The two coefficients, S_0 and B_0 , are determined from a plot of the experimental flux versus the mean pressure (Figure 3.9), and can be used to estimate the mean pore size with:

$$d_{p} = \frac{32}{3} \frac{S_{0}}{B_{0}} \mu \sqrt{\frac{8RT}{\pi M_{N2}}}$$
(3.8)

The tortuosity factor is then found with this estimate of d_p , and ε calculated from Eq. (3.5):

$$\tau = \frac{M_{N2}}{RT} \frac{d_p^2 \varepsilon}{32\mu \frac{d_o}{2} \ln \frac{d_o}{d_i}} S_0$$
(3.9)

Note that the outer fiber diameter is used in this equation since the flux, as defined in Eq. (3.6), is based on the outer membrane surface area.


(a)



Figure 3.8: Experiment for measuring pore size and porosity-tortuosity ratio. (a) Experimental setup. (b) Shell-and-tube, hollow-fiber module.



Figure 3.9: Plot of one gas permeation experiment with hollow-fiber module to measure pore size and porosity/tortuosity ratio. Slope, $S_0 = 1.21 \times 10^{-13} \text{ mol m}^{-2} \text{s}^{-1} \text{Pa}^{-2}$ and intercept, $B_0 = 1.59 \times 10^{-7} \text{ kg m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$.

Again, a model-experiment comparison adds confidence to the membrane parameter measurements and the membrane transport models. Sirkar and Li [101, 102] used the Oxyphan hollow fibers in modules supplied by AMT. With their heat and mass flux data, the membrane mass transfer coefficients can be calculated for three of their Oxyphan-membrane modules using a log-mean vapor pressure difference and a calculated temperature polarization coefficient. This results in membrane mass transport coefficients of 87, 95, and 108 (x 10^{-6} kg m⁻² s⁻¹ kPa⁻¹) for the three modules, which is near 105 (x 10^{-6} kg m⁻² s⁻¹ kPa⁻¹), the value predicted with the equations in Chapter 4.

3.3 Characterizing a membrane heat pump

In this thesis, the term characterizing refers to quantitatively describing the design, the operating conditions, and the performance of a membrane heat pump. The design is described with a productivity-selectivity tradeoff, similar to methods used for mass transfer in membrane separations. A modified NTU-effectiveness method from heat exchangers describes the operating conditions. And methods from absorption heat pumps measure the performance. The approach starts with simplifying the governing equations and identifying dimensionless groups.

An energy balance on a cross section of fluid (Figure 3.10) leads to the following equations for the solution and water flows:

$$\dot{m}_{s}c_{p,s}\frac{dT_{s}}{dx} = KW(H_{v} + \Delta H_{mix})(p_{v,w} - p_{v,s}) + UW(T_{w} - T_{s})$$
(3.10)

$$\dot{m}_{w}c_{p,w}\frac{dT_{w}}{dx} = -KWH_{v}(p_{v,w} - p_{v,s}) - UW(T_{w} - T_{s})$$
(3.11)

where the subscripts *w* and *s* refer to water and solution, c_p is the specific heat, *W* the width of the module perpendicular to the flow, H_v the enthalpy of water vapor at the water temperature (T_w) , and *K* and *U* the overall mass and heat transfer coefficients between the two flows. These last two coefficients are the parameters characterizing each design. The mass transfer coefficient is the mass flux per vapor pressure driving force [kg/m²-s-kPa] while the heat transfer coefficient is the heat flux per temperature driving force [W/m²-K]. They control the magnitude of the two terms on the right hand sides of these equations. During typical operation, the first term (latent energy transfer) is positive since $p_{v,w} > p_{v,s}$, while the second term (sensible energy transfer) is negative since $T_s > T_w$. The temperature change of the solution and water flows is controlled by the balance of these two energy transfers. Note that the right-hand sides of these equations differ not only in the sign in front of each term, but also by the heat of mixing, ΔH_{mix} , on the solution side. The heat of mixing is released during the exothermal mixing process as vapor flux through the membrane dilutes the aqueous solution. The heat of mixing is based on the energy of both ion-dipole and hydrogen bonds that are broken and formed during this dilution process, and it depends on both the temperature and the mass fraction of the solution. As a benchmark, at 50°C, ΔH_{mix} is 350 kJ/kg for CaCl₂ at a mass fraction of 0.4 and for LiCl at a mass fraction of 0.5. It decreases as either temperature or mass fraction is reduced. For details, see Conde [94].



Figure 3.10: Control-volume for energy balance on cross-section of solution side flow. Two energy fluxes at the top are heat transfer with the water-side flow.

Three dimensionless numbers from these equations help define the important parameters.

Dividing the latent energy term by the sensible energy term gives:

$$\Pi_{1} = \frac{K(H_{\nu} + \Delta H_{mix})(p_{\nu,w} - p_{\nu,s})}{U(T_{w} - T_{s})} = \frac{K(H_{\nu} + \Delta H_{mix})\Delta p_{\nu}}{U\Delta T}$$
(3.12)

A second dimensionless group is obtained by dividing the solution-flow term by the water-flow term:

$$\Pi_2 = \frac{\dot{m}_s c_{p,s} \Delta T_s}{\dot{m}_w c_{p,w} \Delta T_w}$$
(3.13)

Finally, a third dimensionless group is the ratio of the latent heat transfer to the solution-flow term:

$$\Pi_{3} = \frac{KAH_{\nu}\Delta p_{\nu}}{\dot{m}_{s}c_{p,s}\Delta T_{s}}$$
(3.14)

These dimensionless groups help identify the design parameters, operating parameters, and performance metrics.

3.3.1 Design parameters

Those readers familiar with membrane separations are likely familiar with the tradeoff between selectivity and permeability in membrane separations. The permeability is the volumetric flux divided by the driving potential gradient (e.g., a pressure gradient). The selectivity is the ratio of the permeability of the two gases to be separated. A high selectivity is desired, as this implies a purer, higher-quality product stream. A high permeability is desired, as this implies a smaller, less expensive module to reach a given quantity of the product stream. Thus, the goal is a membrane with high selectivity and permeability; but these quantities are, in general, inversely related [120].

The membrane heat pump process can be looked at in an analogous way. The first dimensionless group (Π_1) can be rearranged to a new parameter: the membrane heat pump selectivity. This term approximates the potential temperature lift ($^{\circ}$ C) per vapor-pressure driving force (kPa):

$$\alpha_{\text{selectivity}} = \frac{\Delta T}{\Delta p_{v}} = \frac{KH_{v}}{U}$$
(3.15)

The numerator in the second equality represents the latent energy transfer, the desired quantity, while the denominator represents the sensible energy transfer, the undesired quantity. As an example, if the selectivity is low, most of the latent heat transfer from the water to the solution will return to the now-cooler water, minimizing the temperature lift. The design goal is to maximize this selectivity. However, there is a tradeoff to consider between this selectivity and the permeability. The permeability is modified to be the specific heating capacity (W/m^2-kPa) of the device, which is referred to as the productivity:

$$Q_{prod} = KH_{v} \tag{3.16}$$

The selectivity relates to the performance (the temperature lift) of the device, while the productivity relates to the size of the device. The productivity is the heating capacity (W) for a given size device (m^2) per vapor-pressure driving force (kPa). If the productivity decreases, either more membrane area or an absorbent with a lower vapor pressure is required to maintain a given capacity. For example, for a required capacity of 1 kW and a vapor pressure difference of 1 kPa, a device with a heating capacity of 100 W/m²-kPa requires 10 m² of transfer area, while a device with a heating capacity of 50 W/m²-kPa requires 20 m² of transfer area. Thus, the second device is twice as large and likely nearly twice as expensive.

3.3.2 Operating parameters

The two operating parameters of interest here are the absorbent and refrigerant flow rates. In a complete system, there will be other operating parameters, but the focus here is on the evaporator-absorber component. To characterize the flow rates, this study modifies the effectiveness-NTU method used for heat exchangers. Before discussing this modified method, the next few paragraphs discuss the original method for heat exchangers.

In the original method [121], a heat exchanger's effectiveness is a function of just two parameters: the dimensionless number of transfer units (NTU) and the ratio of the flow-weighted heat capacities of the two fluids. The NTU represents the size, and therefore cost, of a heat exchanger. It is defined as the overall thermal conductance divided by the smaller heat capacity rate:

$$NTU_{HX} = \frac{UA}{\left(\dot{n}c_p\right)_{\min}}$$
(3.17)

where the thermal conductance is the overall heat transfer coefficient (U) times the total exchanger area (A), both properties of the heat exchanger device. The denominator is the fluid's mass flow rate (\dot{m}) times its specific heat capacity (c_p), properties of the fluid and the operating conditions. The subscript *min* indicates that the smaller of the two fluid's heat capacity rates should be used.

As discussed by Shah and Sekulic [122], the NTU is the ratio of the heat transfer rate between the two fluids to the rate of enthalpy change of the smaller heat capacity rate fluid. It can be thought of as a non-dimensional heat transfer size of the exchanger. It is not actually the size of the exchanger, which is simply the surface area *A*, but for a specific application, the ratio $U/(\dot{mc}_p)_{min}$ is relatively constant, and then a higher NTU represents a larger physical size.

Regardless of how it is interpreted, increasing the NTU increases the heat exchanger effectiveness, which is defined as the ratio of the actual heat transfer rate to the maximum possible heat transfer rate:

$$\varepsilon_{\rm HX} = \frac{q}{q_{\rm max}} = \frac{\dot{m}c_{p,h}(T_{h,out} - T_{h,in})}{\left(\dot{m}c_p\right)_{\rm min}(T_{h,in} - T_{c,in})}$$
(3.18)

where $T_{h,out}$ is the outlet of the hot fluid, $T_{h,in}$ and $T_{c,in}$ the inlet temperatures of the hot and cold fluids, respectively. The effectiveness is discussed in more detail in the next section on the performance metrics used for a membrane heat pump.

The ratio of flow-weighted heat capacities, referred to as the heat capacity rate ratio in heat transfer texts [121], is:

$$R_{C,HX} = \frac{\left(\dot{m}c_{p}\right)_{1}}{\left(\dot{m}c_{p}\right)_{2}} = \frac{\Delta T_{2}}{\Delta T_{1}}$$
(3.19)

where the subscripts 1 and 2 represent each fluid. Neglecting viscous heating and any losses to the environment, this ratio is also the ratio of the change in temperature of the two fluids, as shown in the second equality in Eq. (3.19). For a given heat exchanger, the NTU is varied with the flow rate of the minimum heat capacity fluid. And for a given NTU, the ratio of flow-weighted heat capacities is varied with the flow rate of the higher-heat-capacity fluid.

In a similar way, the three dimensionless numbers for the heat pump are used to derive a new modified effectiveness-NTU method, where the effectiveness is, again, a function of both the NTU and the ratio of flow-weighted heat capacities.

Defining NTU for a membrane heat pump is not straightforward. Using a direct analogy to the heat exchanger NTU, the heat pump NTU should be:

$$NTU_{\text{dimensional}} = \frac{KA(H_v + \Delta H_{mix})}{\dot{m}c_p}$$
(3.20)

However, this is not dimensionless but rather has the dimensions of a vapor pressure difference divided by a temperature difference (kPa/K). Adding characteristic values for the vapor pressure and temperature differences remedies this:

$$NTU = \frac{KA(H_v + \Delta H_{mix})\Delta p_{v,LM}}{\dot{m}c_p \Delta T_{lift,max}}$$
(3.21)

which can be recognized as the third dimensionless number (Π_3) derived from the governing equations. This is the ratio of two energy transfers: the latent energy transfer to the amount of energy transfer required to reach the maximum temperature lift. Ignoring sensible heat transfer across the membrane, temperature and concentration polarization, and the reduction in concentration of the solution from the inlet to the outlet, the maximum temperature lift is reached at an NTU of one. This definition is not ideal, as the vapor pressure difference in the numerator is not a constant; it changes as the flow rate in the denominator changes. But it normalizes the solution mass flow rate for devices with different surface areas. For a given membrane heat pump module, the NTU is varied by the flow rate of the absorbent. The ratio of flow-weighted heat capacities then represents the water flow rate. The ratio of flow-weighted heat capacities for the heat pump is:

$$R_{C} = \frac{\left(\dot{m}c_{p}\right)_{s}}{\left(\dot{m}c_{p}\right)_{w}} \approx \frac{\Delta T_{w}}{\Delta T_{s}}$$
(3.22)

which is a slight modification to the second dimensionless number (Π_2) derived from the governing equations. It is approximately equal to the change in temperature of the water to the change in temperature of the solution, but not exactly due to the exothermic mixing in the solution. This ratio should be minimized to maximize the solution temperature. In other words, the water flow rate should be set high so the water temperature remains relatively constant. Otherwise, if the water flow rate is too low, the exiting water temperature is low. This is undesirable. Lower water temperatures reduce the water vapor pressure which reduces the driving force for mass transfer. It also increases the driving force for sensible heat transfer. Thus,

lower water mass flow rates lead to less latent heat transfer and more sensible heat transfer, both of which reduce the temperature lift.

Note that the above analysis is for heating applications. For cooling, the analysis above holds except that 'water flow rate' and 'solution flow rate' should be switched. The membrane heat pump can be used for cooling, but this is not explored in depth in the remaining chapters of this thesis.

3.3.3 Performance metrics

For the heat pump, the effectiveness is defined the same as Eq. (3.18) except that the temperature difference in the denominator needs to be modified. As Eq. (3.18) is written, the temperature difference in the denominator is irrelevant, and in fact with equal water and solution inlet temperatures, this temperature difference is zero. Using the maximum temperature lift (Eq. 3.3) to replace this temperature difference, and assuming that the solution's heat capacity (\dot{mc}_p) is lower than that of water, the heat pump effectiveness is:

$$\varepsilon_{\rm HP} = \frac{\Delta T_{lift}}{\Delta T_{lift,\rm max}}$$
(3.23)

Recall that the temperature lift is defined as $T_{s,out} - T_{w,in}$.

One tradeoff mentioned before is the design tradeoff of the selectivity versus the productivity. There is an additional tradeoff related to the operation of the heat pump. Lowering the solution flow rate increases NTU and results in higher temperature lifts. This higher temperature lift is traded off with the efficiency of the process. The efficiency is defined as the fraction of total latent energy transfer that actually increases the solution temperature:

$$\eta = \frac{\dot{m}_{s}c_{p,s}\Delta T_{\text{lift,actual}}}{KA(H_{v} + \Delta H_{mix})\Delta p_{v,LM}}$$
(3.24)

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The usefulness of the salt solution decreases after passing through the membrane heat pump since the concentration decreases, and therefore the vapor pressure increases. The efficiency is a measure of how efficiently the heat pump is using the concentrated solution. The efficiency would be 100% if there were no conduction losses from the solution back to the water.

As they are defined, the efficiency and effectiveness are related to the NTU as follows: $NTU = \frac{\varepsilon}{\eta}$ (3.25)

Thus, by definition, there is a tradeoff between effectiveness and efficiency when changing the NTU. This is discussed in more detail in Section 5.2.

3.3.4 Asymptotic temperature lift: Analytical solution

Before explaining the detailed nodal model in Section 4.1, a much simpler analytical approach calculates the asymptotic temperature lift. The asymptotic temperature lift is the maximum attainable for a specific device configuration. This newly developed analytical solution shows the importance of each term with a single equation, which gives insight into the design without the use of a complex finite difference model. However, the analytical solution is limited by the assumptions required to solve the differential equations. Referring to Figure 3.10, these assumptions are:

- 1. A high water flow rate leading to a constant water temperature ($\delta T_w/\delta x = 0$)
- 2. Temperature variation limited only to the axial direction $(\delta T/\delta y = \delta T/\delta z = 0)$
- 3. Constant salt mass fraction $(\delta \omega / \delta y = \delta \omega / \delta z = \delta \omega / \delta x = 0)$
- 4. Constant physical properties (a_s, c_p, H_v) and transport coefficients (K, U)
- 5. Negligible heat of mixing
- 6. Constant flow rates in both streams

With the first assumption, Eq. (3.11) is no longer necessary, and the focus is on Eq. (3.10). Even with this and the other assumptions, solving Eq. (3.10) is difficult due to the non-linear relationship between the vapor pressure and the temperature. The vapor pressure above the water can be estimated with the Antoine Equation:

$$p_{v,w} = \exp\left(A + \frac{B}{T_w + C}\right) \tag{3.26}$$

where for water: A=23.478, B = -3984.9, and C = -39.724 (for T_w in K and $p_{v,w}$ in Pa). This is easily calculated since the water temperature is constant. The vapor pressure above the absorbent solution can be calculated in a similar way by adding the solution's water activity:

$$p_{v,s} = a_s \exp\left(A + \frac{B}{T_s + C}\right) \tag{3.27}$$

This is not constant since T_s is changing along the flow. Inserting it into Eq. (3.10) results in a differential equation with no closed-form solution. The differential equation cannot be simplified because of the T_s inside the exponential in Eq. (3.27). An alternative is to approximate the solution vapor pressure with a linear relation:

$$p_{v,s} = a_s p_{v,w} + \frac{dp_{v,s}}{dT} \left(T_s - T_w \right)$$
(3.28)

where the differential, $dp_{v,s}/dT$, can be approximated with the Clausius-Clapeyron equation:

$$\frac{dp_{v,s}}{dT} = \frac{\Delta H_{vap} a_s p_{v,w}}{(R/M)T_w^2}$$
(3.29)

This linear approximation breaks down when the temperature difference $(T_s - T_w)$ is large. Section 5.3.1 assesses the accuracy of this approximation as well as the above assumptions, by comparing the analytical solution to the temperature lift predicted by the finite difference model. These assumptions and approximations simplify the problem to an ordinary differential equation:

$$\frac{dT_s}{dx} = \frac{KWH_v}{\dot{m}c_p} \left(p_{v,w} - a_s p_{v,w} - \frac{dp_{v,s}}{dT} \left(T_s - T_w \right) \right) + \frac{UW}{\dot{m}c_p} \left(T_w - T_s \right)$$
(3.30)

Setting $T'_s = T_s - T_w$, gives:

$$\frac{dT'_s}{dx} + \left(\frac{KWH_v}{\dot{m}c_p}\frac{dp_{v,s}}{dT} + \frac{UW}{\dot{m}c_p}\right)T'_s = \frac{KWH_v}{\dot{m}c_p}p_{v,w}(1-a_s)$$
(3.31)

This can be seen as a linear ordinary differential equation for this modified variable when written as:

$$\frac{dT'_s}{dx} + \alpha_1 T'_s = \alpha_2 \tag{3.32}$$

with the two new coefficients defined as:

$$\alpha_1 = \frac{KWH_v}{\dot{m}c_p} \frac{dp_{v,s}}{dT} + \frac{UW}{\dot{m}c_p}$$
(3.33)

$$\alpha_2 = \frac{KWH_v p_{v,w} (1 - a_s)}{\dot{m}c_p}$$
(3.34)

Solving Equation (3.32) gives the solution temperature profile:

$$T_s = T_w + \frac{\alpha_2}{\alpha_1} \left[1 - \exp\left(-\alpha_1 x\right) \right].$$
(3.35)

Near the end of the channel, the latent heat flux carried with the vapor matches the sensible heat flux due to the temperature gradient. At this point, $dT'_s/dx = 0$, and therefore from Equation (3.32):

$$\alpha_1 T'_s = \alpha_2 \tag{3.36}$$

The asymptotic temperature lift is defined as this temperature difference, T'_s , when $dT'_s/dx = 0$:

$$\Delta T_{\infty} = \frac{\alpha_2}{\alpha_1} = \frac{\frac{KH_{\nu}}{U} p_{\nu,w} (1 - a_s)}{1 + \frac{KH_{\nu}}{U} \frac{dp_{\nu,s}}{dT}}$$
(3.37)

Using Equation (3.27) to replace $dp_{v,s}/dT$, and ignoring the ~10% difference between the liquidwater enthalpy and the enthalpy of vaporization, this equation is rewritten as:

$$\Delta T_{\infty} = \frac{\frac{K\Delta H_{vap}}{U} p_{v,w} (1 - a_s)}{1 + \frac{K\Delta H_{vap}^2}{U} \frac{p_{v,w} a_s}{(R/M) T_w^2}}$$
(3.38)

Note that this neglects any dependence of the activity on temperature, which is a reasonable approximation for the salt solutions considered here (see [94]). It also neglects the change in the solution concentration from the inlet to the outlet of the module. Similar to the equilibrium temperature difference, three of the important parameters in this equation are the enthalpy of vaporization, the solution activity, and the water temperature. The temperature is also inherent in the strongly temperature-dependent vapor pressure. Two parameters not in the maximum temperature lift equation but present in Eq. (3.38) are the overall mass and heat transfer coefficients (K and U). These are the variables the designer controls in the selectivity equation (KH_v/U). Methods in the next chapter estimate these two parameters.

CHAPTER 4 Modeling¹

This chapter details the numerical model in two parts. First, it outlines a set of finite difference equations for a one-dimensional counter-flow model and a two-dimensional cross-flow model. Second, it presents the transport equations for the membranes, air gap, and boundary layers for the flat-sheet geometry and for the hollow-fiber geometry.

4.1 **Finite-difference models**

This section develops two finite-difference models: one for a counter-flow device and one for a cross-flow device. The equations are applicable for any of the flat-sheet and hollowfiber designs described in the previous chapter. Here, though, the counter-flow equations are used for a theoretical, flat-sheet design and the cross-flow equations for the hollow-fiber prototype designs. Note that this analysis relaxes the assumptions for the analytical solution from the previous chapter.

4.1.1 Counter-flow equations

The discretized equations for mass, energy, and species for the counter-flow model are:

$$J_{v,i} dA_{i} = \dot{m}_{s,i} - \dot{m}_{s,i-1} = \dot{m}_{w,i} - \dot{m}_{w,i-1} \qquad i = 1 \text{ to } N_{\text{nodes}}$$
(4.1)

$$q_{w,i}'' dA_{i} = \left(\dot{m}_{w} c_{p,w} T_{w,b}\right)_{i} - \left(\dot{m}_{w} c_{p,w} T_{w,b}\right)_{i-1} \qquad i = 1 \text{ to } N_{\text{nodes}}$$
(4.2)

$$q_{s,i}'' dA_{i} = (\dot{m}_{s} c_{p,s} T_{s,b})_{i} - (\dot{m}_{s} c_{p,s} T_{s,b})_{i-1} \qquad i = 1 \text{ to } N_{\text{nodes}}$$
(4.3)

$$0 = m_{s,i} (\omega_{s,b})_{i} - m_{s,i-1} (\omega_{s,b})_{i-1}$$

 $i = 1 \text{ to } N_{nodes}$ (4.4)

¹ Much of the work in this Chapter was published in two Journal of Membrane Science articles:

^{1.} Woods, J., J. Pellegrino, E. Kozubal, S. Slayzak, and J. Burch, Modeling of a membrane-based absorption heat pump. Journal of Membrane Science, 2009. 337(1-2): p. 113-124.

Woods, J., J. Pellegrino, E. Kozubal, and J. Burch, Design and experimental characterization of a membrane-based absorption heat pump. Journal of Membrane Science. In Press, Corrected Proof. DOI: 10.1016/j.memsci.2010.11.012.

where the subscript b represents the bulk flow condition, and J_v is the vapor mass flux. The subscript i is the node in the solution-flow direction; so the solution flows from i=1 to i= N_{nodes} and the water flows in counter-flow from i= N_{nodes} to i=1. To obtain co-current flow equations, multiply the right-hand side of the water-side equations by negative one. Note that the equations for the heat flux *from* the water side (q''_w) and *to* the solution side (q''_s) differ by the heat of mixing of the salt solution, and that in Eq. (4.4), the zero on the left hand side implies the membranes are completely impermeable to salt.

The differential area is variable since the nodal density is not constant and equals:

$$dA_{\rm i} = (N_{\rm rows} - 1)Wdx_{\rm i} \tag{16}$$

where *W* is the width of the module, the $(N_{rows} - 1)$ term accounts for the transport between all of the channel pairs, and dx_i is the non-constant node size. The nodes are denser near the inlets where the temperature gradients are larger, but the average size is equal to the length of the module divided by the number of nodes.

4.1.2 Cross-flow equations

For the cross-flow configuration, the discretized mass, energy, and species equations are:

$$J_{v,i,j}dA_{i,j} = \dot{m}_{s,i,j} - \dot{m}_{s,i-1,j} = \dot{m}_{w,i,j-1} - \dot{m}_{w,i,j} \qquad i = 1 \text{ to } N_{\text{nodes}}, j = 1 \text{ to } N_{\text{nodes}} \qquad (4.5)$$

$$q''_{w,i,j}dA_{i,j} = \left(\dot{m}_{w}c_{p,w}T_{w,b}\right)_{i,j} - \left(\dot{m}_{w}c_{p,w}T_{w,b}\right)_{i,j-1} \qquad i = 1 \text{ to } N_{\text{nodes}}, j = 1 \text{ to } N_{\text{nodes}} \qquad (4.6)$$

$$q_{s,i,j}'' dA_{i,j} = \left(\dot{m}_{s} c_{p,s} T_{s,b}\right)_{i,j} - \left(\dot{m}_{s} c_{p,s} T_{s,b}\right)_{i-1,j} \qquad i = 1 \text{ to } N_{\text{nodes}}, j = 1 \text{ to } N_{\text{nodes}} \qquad (4.7)$$

$$0 = m_{s,i,j} \left(\omega_{s,b} \right)_{i,j} - m_{s,i-1,j} \left(\omega_{s,b} \right)_{i-1,j}$$

 $i = 1 \text{ to } N_{\text{nodes}}, j = 1 \text{ to } N_{\text{nodes}}$ (4.8)

where the subscripts i and j are the nodes in the solution and water-flow directions, respectively. The differential area is variable since the nodal density is not constant and equals:

$$dA_{i,j} = (N_{\text{rows}} - 1)dx_{i,j}dy_{i,j}$$
(4.9)

where $dx_{i,j}$ and $dy_{i,j}$ are the non-constant node sizes in the solution and water directions,

respectively. This differential area is the planar area between the fibers, as opposed to the total *membrane* area, which has implications for the way the transport coefficients for the hollow-fiber design are defined in Section 4.2. The total planar area for each row is defined as:

$$A_{\text{planar}} = N_{\text{fibers}} L_{\text{fiber}} t \tag{4.10}$$

where L_{fiber} is the length of the fiber, N_{fibers} the number of fibers per row, and the fiber spacing, *t*, is defined in Figure 4.2 below.

4.1.3 Transport equations

The equations for mass and heat transport between the two flows are the same for both the counter-flow model and the cross-flow model. With the nodal subscripts dropped for simplicity, these equations are:

$$J_{v} = K_{0} (p_{v,w,m} - p_{v,s,m})$$
(4.11)

$$q''_{\rm w} = -J_{\rm v}H_{\rm v} + U_0 (T_{\rm s,m} - T_{\rm w,m})$$
(4.12)

$$q_{\rm s}'' = J_{\rm v} (H_{\rm v} + H_{\rm mix}) - U_0 (T_{\rm s,m} - T_{\rm w,m})$$
(4.13)

where the subscript m represents the membrane-liquid interface. The transport coefficients are calculated for each node with:

$$K_{0} = \left[\frac{1}{K_{\text{mem}}} + \frac{1}{K_{\text{gap}}} + \frac{1}{K_{\text{mem}}}\right]^{-1}$$
(4.14)

$$U_{0} = \left[\frac{1}{h_{\text{mem}}} + \frac{1}{h_{\text{gap}}} + \frac{1}{h_{\text{mem}}}\right]^{-1}$$
(4.15)

where K_{gap} and K_{mem} are the mass transfer coefficients for the air gap and the membrane, and h_{gap} and h_{mem} the heat transfer coefficients for the air gap and membrane. Note that K_0 and U_0 , which are based on the temperatures and vapor pressures at the membrane-liquid interfaces, are not the same as *K* and *U* from Chapter 3, which are based on the bulk temperature and vapor-pressure differences. These bulk and membrane-liquid interface temperatures are related with:

$$q''_{\rm w} = h_{\rm w} \left(T_{\rm w,m} - T_{\rm w,b} \right) \tag{4.16}$$

$$q_{\rm s}'' = h_{\rm s} \left(T_{\rm s,m} - T_{\rm s,b} \right) \tag{4.17}$$

where h_w and h_s are the convective heat transfer coefficients in the water and solution flows. Using the stagnant film model, which is based on the steady-state differential mass balance with 100% rejection of the salt (for details, see [123]), the mass fractions at the bulk and the membrane-liquid interface are related with:

$$\frac{\omega_{\rm s,m}}{\omega_{\rm s,b}} = \exp\left(\frac{-J_{\rm v}}{k_{\rm m}\rho_{\rm s}}\right) \tag{4.18}$$

where k_m is the solution-flow mass transfer coefficient and ρ_s the density of the salt solution.

Figure 4.1 shows the resistance networks for both heat and mass transfer. Due to the vapor-pressure gradient, mass moves from left to right across the membrane and air gap. The mass-transfer resistance for the boundary layer is considered separately from these resistances since it is based on salt mass fraction instead of water vapor pressure. Heat transfer is from right to left across the membranes and air-gap, but from left to right across the boundary layers. The overall heat transfer is from left to right due to the latent energy carried with the vapor, which is removed and added at the membrane-liquid interfaces. Equations for the transport coefficients in each resistance in Figure 4.1 are outlined in the next section.



Figure 4.1: Resistance networks for (a) mass transfer and (b) heat transfer. Nomenclature is explained in the text. Mass transfer and cumulative heat transfer are from left to right. Sensible heat transfer across membranes and air gap from right to left.

4.2 Transport coefficients

The equations in this section estimate the transport coefficients for each resistance in Figure 4.1. In addition to explaining the equations, this section also includes assumptions and citations to relevant literature. Readers uninterested in the origin and derivation of these equations can skip to Section 4.2.10 titled 'Transport coefficients: summary.' In the following sections, both flat-sheet and hollow-fiber coefficients are developed. The notation for each is shown in Figure 4.2.



Figure 4.2: Notation for (a) flat-sheet and (b) hollow-fiber geometry. d_{gap} is the air gap width, δ_{mem} the membrane thickness, z the fiber row spacing, d_o the outer fiber diameter, d_i the inner fiber diameter, and t the fiber spacing. BL = 'boundary layer' region.

4.2.1 Membrane: mass transfer coefficient

Mass transfer through porous membranes is often calculated with the dusty gas model, particularly in the membrane distillation literature [17, 18]. The dusty gas model is based on the equations for a multi-component gas mixture, where the membrane is considered as one of the components of this gas mixture, made up of giant molecules like dust in a gas. J.C. Maxwell [124] first developed this model in 1860 and more recently, Mason and Malinauskas [125] covered it in a detailed book in 1983. The mass transport equations are derived by applying the kinetic theory of gases to this multi-component mixture of gas molecules and fixed-in-space solid molecules. The total momentum transferred to a single molecule is the sum of the momentum transferred to the wall (the "dusty gas") and to the other molecules. The adaptation here, which is often used in membrane distillation modeling [17, 18], considers three mechanisms for mass transfer: Knudsen or free-molecular flow, viscous flow, and molecular or ordinary diffusion. Thermal, pressure, and surface diffusion are assumed negligible [18]. Knudsen and molecular diffusion are in series since the total momentum transfer is the sum of momentum transferred to the walls (Knudsen) and to other molecules (molecular diffusion). The viscous flux and diffusive flux are added directly (in parallel), since there are no diffusion terms in the Navier-Stokes equations and no viscous terms in the Stefan-Maxwell diffusion equations. For details on these equations, see Section A.3.1 in Appendix A.

In the heat pump, there is a binary mixture of water vapor and air, which is assumed to behave as an ideal gas. Assuming constant total pressure in the membrane pores and negligible air flux results in the Bosanquet equation [126] for the vapor mass flux:

$$n_{\nu} = -\frac{M_{\nu}}{RT} \left[\frac{1}{D_{\rm K}} + \frac{p_a}{pD_{\rm M}} \right]^{-1} \nabla p_{\nu} \tag{4.19}$$

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where $D_{\rm M}$ and $D_{\rm K}$ are the molecular-diffusion and Knudsen-flow transport coefficients for water vapor, and $p_{\rm a}$ the partial pressure of air.

Assuming cylindrical pores, the molecular-diffusion and Knudsen-flow transport coefficients for water vapor are:

$$D_{\rm M} = \frac{\varepsilon}{\tau} D_{\nu a} \tag{4.20}$$

$$D_{\rm K} = \frac{\varepsilon}{\tau} \frac{d_p}{3} \sqrt{\frac{8RT}{\pi M_w}}$$
(4.21)

where D_{va} is the binary diffusion coefficient for water vapor in air. As is often done in the membrane-distillation literature, we assume that the deviation of pores from being straight, cylindrical, and non-interconnected is effectively captured in the tortuosity factor (τ). Combining Eqs. (4.19-4.21) and converting the vapor-pressure gradient to a vapor pressure difference divided by the membrane thickness (δ_{mem}), the membrane transport coefficient is:

$$K_{\rm mem} = \frac{M_{\rm w}}{RT} \frac{1}{\delta_{\rm mem}} \frac{\varepsilon}{\tau} \left[\frac{3}{d_p} \sqrt{\frac{\pi M_{\rm w}}{8RT}} + \frac{p_{a,\rm LM}}{pD_{\rm va}} \right]^{-1}$$
(4.22)

which, as stated before, is a series combination of Knudsen diffusion (first term) and molecular diffusion (second term). Since this equation is based on a vapor-pressure difference, rather than a gradient, it uses the log-mean pressure of air, $p_{a,LM}$. The unknown membrane parameters in this equation (ε , τ , d_p , δ_{mem}) are estimated as described in Section 3.2.3.

As that section discussed, Eq. (4.22) assumes that the mean pore size of the membrane accurately represents the distribution of pore sizes actually present in the pores. For viscous flow, which is not present here, the distribution of pore sizes is more important since the flux is proportional to the pore diameter squared. In the case of combined Knudsen-molecular diffusion, the flux is proportional to the pore diameter to an exponent less than one.

The pore-size distribution model in Appendix A estimates the uncertainty in the water vapor flux when neglecting pore-size distribution in the heat pump model. This uncertainty depends on the width of the pore-size distribution and on the mean pore size. The uncertainty for a design using a single membrane, rather than an air gap between two membranes, is less than 20% for all pore sizes, and less than 10% for the 0.2 micron pore size considered here. This is small, but perhaps not negligible. However, as discussed in the next chapter, the design using a single membrane is theoretical and thus it is safe to assume that all pore-size distribution effects are captured in the 'effective' mean pore size. For the design with an air gap, assuming an air gap width of 1 mm, the vapor flux uncertainty due to pore size distribution is less than 5%. For commercially-made membranes, the distribution is likely fairly narrow and this uncertainty less than 2%. In addition, the calculation does not include the effects of temperature or concentration polarization, which reduces this uncertainty. For details, see Appendix A.

4.2.2 Membrane: heat transfer coefficient

The heat transfer coefficient for the membrane is based on equations for heat conduction through porous media. Many equations exist to predict the thermal conductivities of porous materials, but only three common ones are discussed here. The first two are the parallel and series models, which are theoretically the two extremes assuming conduction is the only mechanism present. These equations are:

$$\lambda_{\rm eff} = \varepsilon \,\lambda_{\rm g} + (1 - \varepsilon) \lambda_{\rm polymer} \tag{4.23}$$

for the parallel model and:

$$\lambda_{\rm eff} = \frac{1}{\frac{\varepsilon}{\lambda_{\rm g}} + \frac{(1-\varepsilon)}{\lambda_{\rm polymer}}}$$
(4.24)

for the series model. In these equations, λ_g is the thermal conductivity of the gas in the pores and $\lambda_{polymer}$ is the thermal conductivity of the solid membrane material. The thermal conductivities of common hydrophobic materials used for membranes are between 0.15 W/m-K (polypropylene) and 0.25 W/m-K (PTFE). The heat transfer coefficient is simply this effective thermal conductivity divided by the membrane thickness:

$$h_{\rm mem} = \frac{\lambda_{\rm eff}}{\delta_{\rm mem}} \tag{4.25}$$

Equations (4.23) and (4.24) are plotted in Figure 4.3, along with experimentallymeasured thermal conductivities from the literature, which were measured using indirect methods (membrane distillation experiments) and direct methods (a Lees' Disc method [127]). Table 4.1 lists these experiments.

The indirect method is essentially a membrane distillation experiment, using vapor flux, temperature, and liquid flow rate measurements to infer the membrane conductivity. The uncertainty for this method is high, not only because the conductivity depends on three measurements, but because it also depends on the methods for calculating other transport coefficients. For example, the indirect method calculates an inaccurate conductivity if an inaccurate model is used for the membrane mass transfer coefficient or an inaccurate correlation is used for temperature polarization. The indirect measurements are from several researchers (Table 4.1) and are shown in the open circles in Figure 4.3. In general, this method gives higher thermal conductivities than the other method.

The Lees' Disc method finds the thermal conductivity by directly applying a known heat flux and measuring temperatures. Measurements from Izquirdo-Gil et al. [128, 129] using this method (grey triangles) are lower than most indirect measurements; they are near the minimum extreme of the series model. However, Garcia-Payo and Izquirdo-Gil [130] later found that these

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measurements were in error. The method uses a stack of flat-sheet membranes, but the original study did not consider the gaps of air between each membrane. Factoring in this extra thermal resistance results in the dark circles shown in the figure. This led Garcia-Payo and Izquirdo-Gil [130] to recommend an intermediate model such as the geometric mean, which is:

$$\lambda_{eff} = \lambda_{polymer}^{1-\varepsilon} \lambda_g^{\varepsilon} \tag{4.26}$$

This is the third line shown in Figure 4.3. It matches their data (dark circles) with reasonable accuracy ($R^2 = 0.85$).

The majority of membrane distillation studies use the parallel model [130], although it appears that this over-predicts most experimental measurements (Figure 4.3). This discrepancy between membrane distillation experiments and direct experimental measurements of the thermal conductivity has yet to be resolved, and resolving it is outside the scope of this thesis.

The parametric analysis in Chapter 5 uses the geometric-mean model. The choice of the model is not very important for the air-gap design. For a 1-mm air gap, the parallel model predicts a heat transfer coefficient at most 6% above the geometric mean model, while the series model predicts a heat transfer coefficient 5% below. These worst-case uncertainties are acceptable for the current analysis. However, for the design with no air gap (single-membrane design), the parallel model is up to 60% above the geometric mean model and the series model up to 40% below. These differences are more concerning. For the single-membrane design, the parametric analysis considers all three models (series, geometric mean, and parallel) to gauge the sensitivity of the overall results to the choice of membrane conductivity equation.



Figure 4.3: Comparison of theoretical and experimentally measured membrane thermal conductivities. Indirect measurement using membrane distillation experiments (\circ), Lees Disc experiments from [128, 129] (\blacktriangle), and Lees Disc experiments from [130] (\bullet).

		kexperimental		
3	reference	(W/m-K)	membrane	measurement method ¹
0.62	[129]	0.041	Millipore, PVDF22	Lees Disc
0.62	[130]	0.057	Millipore, PVDF22	Lees Disc
0.62	[131]	0.0835	Millipore, PVDF22	MD experiments
0.66	[128]	0.04	Millipore, PVDF45	Lees Disc
0.66	[130]	0.052	Millipore, PVDF45	Lees Disc
0.66	[131]	0.087	Millipore, PVDF45	MD experiments
0.75	[132]	0.039	Nitto Denko, NTF-1122	MD experiments
0.8	[131]	0.036	Pall, TF200	MD experiments
0.8	[131]	0.0378	Pall, TF450	MD experiments
0.8	[133]	0.043	Pall, TF200	MD experiments
0.8	[134]	0.0432	Pall, TF200	MD experiments
0.8	[135]	0.055	Pall, TF200	MD experiments
0.89	[130]	0.031	Gore, PTFE45	Lees Disc
0.89	[129]	0.027	Gore, PTFE45	Lees Disc
0.9	[130]	0.039	Gore, PTFE20	Lees Disc
0.9	[129]	0.031	Gore, PTFE20	Lees Disc

Table 4.1: Experimental thermal conductivity values from the literature, corresponding to data in Figure 4.3.

 T MD = membrane distillation

4.2.3 Membrane: hollow-fiber modification

The membrane transport coefficients for the hollow-fiber design are derived from the heat flux equation in cylindrical coordinates:

$$q'' = \frac{2k\,\Delta\mathrm{T}}{d_o\,\ln\frac{d_o}{d_\mathrm{i}}}\tag{4.27}$$

All of the heat and mass fluxes in the model are based on the planar area between the rows of fibers (Eq. 4.10). Thus, Eq. (4.27) is multiplied by the half-area of the fibers ($N_{fibers} L_{fiber} \pi d_o/2$) and then divided by the planar area ($N_{fibers} L_{fiber} t$):

$$q'' = \frac{\pi k \Delta T}{t \ln \frac{d_o}{d_i}}$$
(4.28)

where t is the spacing between the fibers (Figure 4.2b). Note that the equation was multiplied by the half-area of the fibers because the model considers heat transfer through each side of the fiber rows separately. The flat sheet transport equations for both heat and mass transfer can be converted to the hollow fiber transport equations by replacing the membrane thickness with:

$$\delta_{\rm mem} = \frac{t \ln \frac{d_{\rm o}}{d_{\rm i}}}{\pi} \tag{4.29}$$

4.2.4 Air-gap: mass transfer coefficient

Mass transfer across the air gap is assumed to take place with negligible natural convection. This is an important assumption. It will be discussed again regarding the hollow-fiber geometry in Section 4.2.7 and regarding experiments in Section 6.3. With no natural convection, the equation for diffusion across the air gap is:

$$K_{gap} = \frac{M_1}{RT} \frac{p}{p_{a,LM}} \frac{D_{va}}{d_{gap,eff}}$$
(4.30)

where $d_{gap,eff}$ is the effective gap thickness. For the flat sheet geometry, this would theoretically be the air-gap width, although membrane bowing would likely reduce this thickness. Izquierdo-Gil et al. [129] developed an experimental method for estimating the effective gap thickness in air-gap membrane distillation. They found that the effective gap thickness under static conditions was 0.9 mm when the gasket between the membranes was 1 mm. Garcia-Payo et al. [136] found that the effective gap thickness also depends on membrane thickness, with the effective gap thickness less for thinner membranes. In this work, membrane bowing is ignored by simply specifying an effective gap thickness for the flat-sheet designs. The effective gap thickness for the hollow-fiber design is discussed in Section 4.2.6.

4.2.5 Air-gap: heat transfer coefficient

Heat transfer across the air gap also assumes negligible natural convection. The heat transport coefficient for the air gap is the sum of conduction and radiation:

$$h_{\rm gap} = \frac{\lambda_{\rm g}}{d_{\rm gap,eff}} + \frac{\sigma_{\rm SB} F_{\rm I-2}}{2/\varepsilon_{\rm rad} - 1} \left(T_1^2 + T_2^2\right) \left(T_1 + T_2\right)$$
(4.31)

where σ_{SB} is the Stefan-Boltzmann constant, T_1 and T_2 the temperatures at the outer-membrane surfaces, ε_{rad} the emissivities of these surfaces, and F_{1-2} the radiation view factor between the surfaces. For the flat sheet case, $d_{gap,eff}$ is simply the air-gap width and F_{1-2} is equal to one. For the hollow-fiber case, these parameters require some additional analysis as discussed in the following section.

4.2.6 Air-gap: hollow-fiber modification

The transport across the air gap in the hollow-fiber case is complicated by the complex cylindrical-planar geometry shown in Figure 4.2b. This work develops a method for predicting the conductive heat transfer and diffusive mass transfer across this complex geometry with the use of an effective gap thickness, which is defined, in general, as:

$$d_{\text{gap,eff}} = \frac{\lambda_{\text{g}} \Delta T}{q''} = \frac{\rho_{g} D_{\text{va}} \Delta x_{\text{v}}}{x_{\text{a,LM}} J_{\text{v}}}$$
(4.32)

where Δx_v is the difference in vapor mass fraction, $x_{a,LM}$ the log-mean mass fraction of air, ρ_g the density of the air-vapor mixture, and ΔT the temperature difference. The fluxes and difference terms are defined between the outer fiber surfaces.

Calculating the effective gap thickness is based on a three-dimensional finite-volume analysis using the computational fluid dynamics package ANSYS[®] Fluent[®]. The mesh is shown in Figure 4.4. The analysis neglects all buoyancy forces and considers only conduction heat

transfer. From the Fluent results, an effective gap thickness is calculated from Eq. (4.32) with ΔT based on the outer-membrane surface temperatures. These are average surface temperatures since the mesh includes the membrane, but the entire membrane is nearly isothermal since its thermal conductivity is an order of magnitude higher than that of air. The ANSYS simulation results are fit to an equation of the form:

$$d_{\text{gap,eff}} = \frac{2t}{a_0 \pi} \ln \left[\frac{2}{\pi} \frac{t}{d_0} \sinh \left(b_0 \frac{\pi}{2} \frac{z}{t} \right) \right]$$
(4.33)

where *t* is the fiber spacer, d_0 the fiber outer diameter, and *z* the distance between the rows ($d_0/2 + d_{gap}$). This equation is based on a conduction shape factor from the heat transfer literature for a parallel row of isothermal cylinders. The dimensionless shape factor, per cylinder, is [137, 138]:

$$S = \frac{\frac{\pi}{2}}{\ln\left[\frac{2}{\pi}\frac{t}{d_{o}}\sinh\left(\frac{\pi}{2}\frac{z}{t}\right)\right]}$$
(4.34)

The effective gap thickness is just the inverse of the conduction shape factor, with the fiber spacing, t, added to Eq. (4.34) to base it on the planar area between the fibers. The two coefficients, a_0 and b_0 , correct the equation for: (1) the inaccuracy of the shape factor at close row spacing [138] and (2) for perpendicular (cross-flow) as opposed to parallel (counter-flow) rows of cylinders. The fitting coefficients are a function of the ratio of the fiber spacing to the fiber diameter:

$$a_0 = A_2 \left(\frac{t}{d_o}\right)^2 + A_1 \left(\frac{t}{d_o}\right) + A_0 \tag{4.35}$$

$$b_0 = B_2 \left(\frac{t}{d_o}\right)^2 + B_1 \left(\frac{t}{d_o}\right) + B_0 \tag{4.36}$$

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The fit is based on ANSYS runs for geometries with $1.1 < t/d_0 < 2$ and $1.2 < z/d_0 < 8$. The geometry in the prototype modules from AMT are $t/d_0 = 1.3$ for each module and $z/d_0 = 2.47$, 2.87, and 3.39 for modules #1, 2, and 3, respectively (Table 3.1). For the second-generation prototype, the values are $t/d_0 = 1.15$ and $z/d_0 = 2.5$ (Table 3.2). Non-linear regression determines the coefficients that minimize the sum of the squares of the errors between the finite-volume runs and Eq. (4.33). These coefficients, shown in Table 4.2, result in a correlation with $R^2 = 0.9989$ with a maximum error of 4.3% for the considered range of t/d_0 and z/d_0 , compared to $R^2 = 0.929$ and a maximum error of 33.2% when using $a_0 = 1$ and $b_0 = 1$ in Eq. (4.33).

Table 4.2: Coefficients for Eqs. (4.35) and (4.36) to calculate effective gap thickness

Coefficients for a ₀	$A_2 = 0.2258$	$A_1 = -0.3642$	$A_0 = 1.1244$
Coefficients for b ₀	$B_2 = 0.1852$	$B_1 = -0.2911$	$B_0 = 1.0310$



Figure 4.4: Meshed geometry for Fluent runs for conduction shape factor analysis.

Like the effective gap thickness, the radiation view factor is also complicated by the complex hollow fiber geometry. It is based on a relation from Hottel [139] for a view factor from a vertical plane (subscript 0) to a vertical row of parallel cylinders (subscript 1):

$$F_{0-1} = 1 - \left(1 - D^2\right)^{1/2} + D \tan^{-1} \left(\frac{1 - D^2}{D^2}\right)^{1/2} \text{ where } D = \frac{d_o}{t}$$
(4.37)

This is transformed into a view factor for one row of cylinders to an infinite plane with the relation (see [121]):

$$A_0 F_{0-1} = A_1 F_{1-0} \tag{4.38}$$

to obtain:

$$F_{1-0} = \frac{t}{\pi \, d_{\rm o}} F_{0-1} \tag{4.39}$$

Combining this view factor with the view factor for a plane to a second row of cylinders

(subscript 2) results in:

$$F_{1-2} = \frac{t}{\pi \, d_{\rm o}} F_{0-1}^2 \tag{4.40}$$

This is then modified to base the view factor on the total planar area between the fibers as opposed to the membrane surface area:

$$F_{1-2} = F_{0-1}^{2} = \left[1 - \left(1 - D^{2}\right)^{1/2} + D \tan^{-1} \left(\frac{1 - D^{2}}{D^{2}}\right)^{1/2}\right]^{2}$$
(4.41)

Note that although the spaces between the fibers in each row allow radiation between nonadjacent rows, the second row contains the same fluid as the original row, and is thus excluded,

and the transfer through to the third row is assumed negligible for this cross-flow arrangement.

4.2.7 Air gap: assumption of negligible natural convection

The analysis above assumes negligible natural convection. This is consistent with Rayleigh numbers computed for this geometry based on both the fiber diameter ($Ra_D = 0.09$) and based on the distance between the rows ($Ra_z = 3.5$), which are well below the critical value of Ra ~ 10^3 for a thin, horizontal cavity [121]. Additional Fluent simulations with temperature dependent density also showed natural convection to be negligible for the module in both horizontal and vertical orientations (Appendix B). This analysis is conservative by assuming temperature differences across the air gap of 20°C. Figure 4.5 shows that natural convection is always present for the vertical orientation, as expected, but is not present until reaching a critical Rayleigh number (~ 10^3) for the horizontal orientation. For air gaps considered here (~ 1 mm), natural convection is negligible in both orientations. Experimental tests on module #3 in different orientations reinforced this conclusion, as discussed in Section 6.3.



Figure 4.5: Increase in heat transfer due to natural convection in the air gap over the conductiononly case for horizontal and vertical orientations. Natural convection in both cases negligible for prototype geometry ($d_{gap} = 0.9$ mm). Heat transfer in vertical orientation increases continuously with gap width due to natural convection, while heat transfer in horizontal orientation stays near conduction-only value until reaching the critical Rayleigh number near a gap width of 10 mm. $z/d_o = 3$ and $t/d_o = 1.5$.

4.2.8 Temperature and concentration polarization

The convective heat and mass transport in the flows, often referred to as temperature and concentration polarization, is based on developing-flow correlations for the Nusselt (Nu) and Sherwood (Sh) numbers. From these Nusselt numbers, the water and solution heat transfer coefficients in the flat-sheet design are:

$$h_{\rm w} = \frac{{\rm Nu}\lambda_{\rm w}}{d_{\rm h}} \qquad \qquad h_{\rm s} = \frac{{\rm Nu}\lambda_{\rm s}}{d_{\rm h}} \tag{4.42}$$

From the Sherwood number, the solution mass transfer coefficient is:

$$k_{\rm m} = \frac{{\rm Sh}D_{\rm sw}}{d_h} \tag{4.43}$$

where D_{sw} is the binary diffusion coefficient of the salt in water. Different equations apply to the hollow-fiber design:

$$h_{\rm w} = \frac{{\rm Nu}\lambda_{\rm w}\pi}{2t} \qquad \qquad h_{\rm s} = \frac{{\rm Nu}\lambda_{\rm s}\pi}{2t} \qquad \qquad k_{\rm m} = \frac{{\rm Sh}D_{\rm sw}\pi}{2t} \qquad (4.44)$$

where a geometric correction factor ($\pi d_i/2t$) modifies the standard cylindrical equations so they are based on the total planar area between the fibers.

The Nusselt and Sherwood number correlations are functions of the thermal Graetz number (Gz_T) and the concentration Graetz number (Gz_M), respectively, which are:

$$Gz_T = \frac{d_h}{x} \operatorname{Re} \operatorname{Pr}$$
 $Gz_M = \frac{d_h}{x} \operatorname{Re} \operatorname{Sc}$ (4.45)

where x is the axial location along the flow, Pr is the Prandtl number, Sc the Schmidt number, and d_h the hydraulic diameter. The correct correlation depends on the boundary conditions at the wall, which are complicated by the simultaneous latent and sensible heat transfer. In other words, the problem is neither constant surface heat flux nor constant surface temperature. Zhang [140] investigated, theoretically, fully developed flow with simultaneous heat and mass transfer in the rectangular ducts of a membrane enthalpy exchanger. He found that for wide channels, the Nusselt number was roughly halfway between the two extremes of constant heat flux (Nu = 8.235) and constant wall temperature (Nu =7.54). Choosing this halfway point gives Nu = 7.9 for the flat-sheet design. Similarly, for the hollow-fiber design, the average between the values for constant heat flux (Nu = 4.37) and constant wall temperature (Nu = 3.66) gives Nu = 4. Zhang found similar results for mass transfer, and thus similar equations apply for the Sherwood number.

If the Graetz number for both heat and mass transfer is less than 50, these constant Nusselt and Sherwood number correlations for fully-developed flow can be used. However, a portion of the flow in the heat pump is developing. This could be a small amount, as is often the case for the thermal boundary layer, or it could be developing over the entire length of the module, as is often the case for the concentration boundary layer. The model simply calculates local Nusselt and Sherwood numbers at each node using a single correlation based on the Graetz number. As the Graetz number approaches zero, the equations approach the fully-developed values mentioned before.

For developing flow, the constant heat flux and constant wall temperature correlations for the Nusselt numbers are based on data from Hornbeck [141] and Shah and London [142], and are also found in general heat transfer references [143, 144]. Assuming the results from Zhang [140] also apply to developing flow, an equation can be fit in between the constant heat flux and constant wall temperature correlations. The result is an equation that uses the same form as the constant heat flux and constant wall temperature correlations, but with different coefficients. For parallel plates, this results in the following Nusselt and Sherwood number correlations:

$$Nu = 7.9 + 0.245 \exp\left(\frac{-200}{Gz_T}\right) G z_T^{\frac{1}{2}}$$
(4.46)

$$Sh = 7.9 + 0.245 \exp\left(\frac{-200}{Gz_M}\right) G z_M^{\frac{1}{2}}$$
(4.47)

Similarly, fitting a line between the constant heat flux and constant temperature correlations for cylindrical tubes gives:
$$Nu = 4 + 0.245 \exp\left(\frac{-40}{Gz_T}\right) Gz_T^{\frac{1}{2}}$$
(4.48)

$$Sh = 4 + 0.245 \exp\left(\frac{-40}{Gz_M}\right) G z_M^{\frac{1}{2}}$$
(4.49)

These are preferred to equations of the form $Nu = (\text{constant})Gz_T^{\frac{1}{3}}$, which are sometimes used in membrane distillation models [128, 135, 145, 146]. This latter form approaches zero as the Graetz number approaches zero. In reality, as the Graetz number approaches zero the flow becomes fully developed, and the Nusselt and Sherwood numbers should approach the fullydeveloped value, which is the case for Eqs. (4.46) to (4.49).

A sensitivity analysis using the finite difference model checks the assumption of using the average between the constant-flux and constant-temperature Nusselt numbers. The analysis found that for the hollow-fiber v.1 prototype, changing the Nusselt number from constant heat flux to constant temperature changed the overall mass transfer coefficient (K), overall heat transfer coefficient (U), and temperature lift by -0.1%, 0.05%, and 0.1% respectively. A similar check calculates the sensitivity from changing the Sherwood number from constant mass flux to constant wall concentration. These same three parameters change by 1%, -0.25%, and 0.7%, respectively. These low sensitivities justify using the average between the constant surface temperature and constant heat flux Nusselt numbers, and the average between the constant surface concentration and constant mass flux Sherwood numbers.

The analysis above assumes these correlations are appropriate for the boundary layers in the heat pump. There are several reasons to suspect that they are not. First, there is mass transfer at the wall that will influence boundary-layer development. Second, on the solution side, low velocity will make axial conduction and diffusion more important. Third, viscous dissipation may be important since the dynamic viscosity of the solution is one to two orders of magnitude higher than that for water. Finally, the exothermic heat of mixing can influence the thermal gradients in the flow. The next section investigates these possible effects with a scaling analysis to determine the importance of each term in the governing equations. Non-negligible terms are investigated further with a CFD analysis. The scaling and CFD analyses showed none of these other effects to be important for the dimensions considered here, although one should proceed with caution when modeling other geometries than those discussed in this thesis.

4.2.9 Scaling analysis of boundary layer flow

Before modeling all the details of the flow with CFD, a scaling analysis finds the negligible terms in the problem's governing equations. Scaling analysis is a systematic method for non-dimensionalizing the variables in these governing equations so their values are of order one [147]. The magnitude of the dimensionless coefficients in front of each term estimates that term's significance.

The remainder of this section presents the governing equations, key assumptions, the final non-dimensionalized form of the equations, and the results of the scaling analysis. Appendix C shows the full analysis. The equations are simplified by considering a flat-sheet geometry, as shown in Figure 4.6, and also by assuming incompressible flow, constant physical properties, and the Boussinesq approximation for natural convection. The effect of variation in physical properties is investigated separately below.



Figure 4.6: Flat-sheet channel geometry used for scaling analysis. The thermal and concentration boundary layer thicknesses, (δ_T and δ_M) are used in the scaling analysis below.

With the above assumptions, the governing equations are:

mass:
$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0$$
 (4.50)

x-mom.:
$$u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = -\frac{1}{\rho}\frac{\partial P}{\partial x} + v\left[\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right] - g_x\beta\left(T - T_{ref}\right) - g_x\beta_M\left(\omega_1 - \omega_{1,ref}\right)$$
 (4.51)

y-mom.:
$$u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y} = -\frac{1}{\rho}\frac{\partial P}{\partial y} + v\left[\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2}\right] - g_y \beta \left(T - T_{ref}\right) - g_y \beta_M \left(\omega_1 - \omega_{1, ref}\right)$$
(4.52)

energy:
$$u\frac{\partial T}{\partial x} + v\frac{\partial T}{\partial y} = \alpha \left[\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2}\right] + \frac{1}{\rho c_p}\dot{q}''' + \frac{\mu}{\rho c_p}\left(\frac{\partial u}{\partial y}\right)^2$$
 (4.53)

species 1:
$$u \frac{\partial \omega_1}{\partial x} + v \frac{\partial \omega_1}{\partial y} = D_{sw} \left[\frac{\partial^2 \omega_1}{\partial x^2} + \frac{\partial^2 \omega_1}{\partial y^2} \right]$$
 (4.54)

In these equations, P is the non-hydrostatic pressure, υ the kinematic viscosity, β the thermal expansion coefficient, β_M the concentration expansion coefficient, α the thermal diffusivity, D_{sw}

the mass diffusivity for salt in water, and \dot{q}''' the internal heat generation from the heat of mixing.

For completeness, the boundary conditions for the above equations are listed here:

at
$$x = 0$$
: $u = U_{in}; v = 0; T = T_{in}; \omega_s = \omega_{s,in}$ (4.55)

at y = -H:
$$u = 0; v = V_{wall}(x) = \frac{K}{\rho_w}(p_{v,\infty} - p_v)$$
 (4.56)

$$-k \frac{dT}{dy} = KH_{vapor} (p_{v,\infty} - p_v) + U(T_{\infty} - T)$$

$$-\rho D_{12} \frac{d\omega_s}{dy} = K (p_{v,\infty} - p_v)$$
at x = L: $u = f_1(y); v = f_2(y); T = f_3(y); \omega_s = f_4(y)$

$$P(L, y) = P_{out}$$
at y = H: $u = 0; v = -V_{wall} (x) = -\frac{K}{\rho_w} (p_{v,\infty} - p_v)$

$$k \frac{dT}{dy} = KH_{vapor} (p_{v,\infty} - p_v) + U(T_{\infty} - T)$$

$$\rho D_{12} \frac{d\omega_s}{dy} = K (p_{v,\infty} - p_v)$$
(4.58)

where U_{in} , T_{in} , and $\omega_{s,in}$ are the inlet velocity, temperature, and mass fraction, $V_{wall}(x)$ is the flux through the wall due to vapor transfer, H_v is the water enthalpy at T_{∞} , $f_1(y)$, $f_2(y)$, $f_3(y)$, and $f_4(y)$ are unknown functions, and P_{out} is the outlet pressure. The analysis uses the following dimensionless variables with unspecified scale factors:

$$x^* = \frac{x}{x_s}; \quad y^* = \frac{y}{y_s}; \quad u^* = \frac{u}{U_0}; \quad v^* = \frac{v}{V_{wall,0}}$$
(4.59)

$$T^* = \frac{T - T_0}{T_s}; \quad \omega_1^* = \frac{\omega_1 - \omega_{1,0}}{\omega_{1,s}}; \quad p_v^* = \frac{p_v - p_{v,\infty}}{p_{v,0} - p_{v,\infty}}$$
(4.60)

$$\left(\frac{\partial u}{\partial x}\right)^* = \frac{x_s}{\Delta U_x} \frac{\partial u}{\partial x}; \quad \left(\frac{\partial u}{\partial y}\right)^* = \frac{y_s}{\Delta U_x} \frac{\partial u}{\partial y} \tag{4.61}$$

$$\left(\frac{\partial v}{\partial x}\right)^* = \frac{x_s}{\Delta V_x} \frac{\partial v}{\partial x}; \quad \left(\frac{\partial v}{\partial y}\right)^* = \frac{x_s}{\Delta V_y} \frac{\partial v}{\partial y}$$
(4.62)

$$\left(\frac{\partial P}{\partial x}\right)^* = \frac{x_s}{\Delta P_x} \frac{\partial P}{\partial x}; \quad \left(\frac{\partial P}{\partial y}\right)^* = \frac{y_s}{\Delta P_y} \frac{\partial P}{\partial y}$$
(4.63)

$$\left(\frac{\partial T}{\partial x}\right)^* = \frac{x_s}{\Delta T_x} \frac{\partial T}{\partial x}; \quad \left(\frac{\partial T}{\partial y}\right)^* = \frac{y_T}{\Delta T_y} \frac{\partial T}{\partial y}$$
(4.64)

$$\left(\frac{\partial \omega_{l}}{\partial x}\right)^{*} = \frac{x_{s}}{\Delta \omega_{l,x}} \frac{\partial \omega}{\partial x}; \quad \left(\frac{\partial \omega_{l}}{\partial y}\right)^{*} = \frac{y_{M}}{\Delta \omega_{l,y}} \frac{\partial \omega}{\partial y}$$
(4.65)

For reasons explained in Appendix C, separate scale factors are used for the variables and their derivatives. Separate scale factors are also used for the y-coordinate dimension in the continuity and momentum (y_s) , energy (y_T) , and species (y_M) equations.

Using a short-hand notation for the rest of this analysis, each dimensionless scaled variable (marked with *) is replaced with one, since each of these terms was scaled to be of order one. The techniques used to simplify the momentum, energy, and species equations are discussed in detail in Appendix C. These are summarized as follows. First, each equation is divided through by the dominant term that must be retained for the problem to maintain physical significance. The other dominant term is then set to one, which sets one of the scale factors. The equations are then simplified using the dimensionless numbers in Table 4.3. This gives the five dimensionless governing equations:

continuity:
$$\frac{\Delta U_x}{L} \sim \frac{\Delta V_y}{H}$$
 (4.66)

x-momentum:
$$\operatorname{Re}_{wall} + \operatorname{Re}_{wall} \sim 1 + \frac{\operatorname{Re}_{wall}}{\operatorname{Re}} \frac{H}{L} + 1 - \frac{Gr_T}{\operatorname{Re}} - \frac{Gr_M}{\operatorname{Re}}$$
 (4.67)

y-momentum:
$$\operatorname{Re} \frac{H}{L} + \operatorname{Re}_{wall} \sim 1 + \frac{\operatorname{Re}_{wall}}{\operatorname{Re}} \frac{H}{L} + 1 - \frac{Gr_T}{\operatorname{Re}_{wall}} - \frac{Gr_M}{\operatorname{Re}_{wall}}$$
 (4.68)

energy:
$$1 + \text{Pe}_{wall} \frac{y_T}{H} \sim \frac{1}{\text{Pe}} \frac{H}{L} + 1 + Sp + Br \frac{H^2}{y_T^2}$$
 (4.69)

species 1:
$$1 + \operatorname{Pe}_{M, wall} \frac{y_M}{H} \sim \frac{1}{\operatorname{Pe}_M} \frac{H}{L} + 1$$
 (4.70)

where ~ signifies on-the-order-of. Based on the entrance lengths for this device, we assume that $y_T = H$ and $y_M \sim L/Pe_M$. For details, see Appendix C.

Table 4.4 shows the dimensionless terms in Eqs. (4.66-4.70) for several module dimensions and operating conditions. If a term is on the order of 10^{-2} or less, neglecting it should give an uncertainty of 1-10%, while neglecting a term on the order of 10^{-3} gives an uncertainty of less than 1%. From the sensitivity analysis in 4.2.8, a 10% uncertainty in the boundary-layer correlation has a small effect on the calculated performance parameters.

Dimensionless number	Definition
Reynolds number	$\operatorname{Re} = \frac{U_0 H}{v}$
Wall Reynolds number	$\operatorname{Re}_{wall} = \frac{V_{wall,0}H}{v}$
Thermal Peclet number	$Pe_T = \operatorname{Re}\operatorname{Pr}$
Solutal Peclet number	$Pe_{M} = \operatorname{Re}\operatorname{Sc}$
Wall thermal Peclet number	$Pe_{wall} = rac{V_{wall,0}H}{lpha}$
Wall solutal Peclet number	$Pe_{M,wall} = \frac{V_{wall,0}H}{D_{12}}$
Sparrow number	$\mathrm{Sp} = \frac{\dot{q}''' H^2}{k \Delta T_y}$
Thermal Grashof number	$Gr_{\rm T} = \frac{g\beta \ \Delta T_y H^3}{v^2}$
Solutal Grashof number	$Gr_{\rm M} = \frac{g\beta_M \Delta \omega_y H^3}{\upsilon^2}$
Brinkman number	$Br = \frac{\mu U_0^2}{k\Delta T_y}$

Table 4.3: Dimensionless numbers for scaling analysis

μ m < u _h < 4000 μ m	II), $500 < 1 < 540$ K, $0.55 < \omega_{\rm s} < 0.55$, 10	$< \mathbf{v}_{\text{wall},0} < 10$	ш
x-momentum		Maximum value	
Re _{wall}	Momentum convection	~10 ⁻⁵	
Re _{wall} /Re(H/L)	Axial momentum diffusion	~10 ⁻⁴	
Gr _⊤ /Re	Thermal buoyancy	~10 ⁻¹	
Gr _M /Re	Solutal buoyancy	~1	
y-momentum			
Re _{wall}	Momentum convection	~10 ⁻⁵	
Re _{wall} /Re*(H/L)	Axial momentum diffusion	~10 ⁻⁴	
Ra _T /Ra _{crit}	Thermal buoyancy	~10 ⁻⁴	
Ra _M /Ra _{crit}	Solutal buoyancy	~10 ⁻²	
energy			
Pe _{wall}	Transverse convection	~10 ⁻³	
1/Pe*H/L	Axial diffusion	~10 ⁻³	
Sp	Heat generation	~10 ⁻¹	
Br	Viscous dissipation	~10 ⁻⁵	
species			
Pe _{M,wall} /Pe _M /(H/L)	Transverse convection	~10 ⁻²	
1/Pe _M *H/L	Axial diffusion	~10 ⁻⁵	

Table 4.4: Maximum values from scaling analysis while varying H, T, ω_s , and $V_{wall,0}$. 0.1 < H < 1 mm (200 μ m < d_h < 4000 μ m), 300 < T < 340 K, 0.35 < ω_s < 0.55, 10⁻⁷ < V _{wall,0} < 10⁻⁶ m/s.

Table 4.4 shows that the terms give uncertainties of less than 10% except for the xmomentum buoyancy terms and the heat generation term. In other words, natural convection could assist or hinder the flow (mixed convection) and the heat generation could alter the shape of the temperature gradient at the wall. Note that the y-momentum buoyancy terms were larger than order one, due to the very low value for the wall Reynolds number ($Re_{wall} \sim 10^{-5}$). However, development of natural convection cells requires the Rayleigh number to be on the order of (or larger than) the critical Rayleigh number. Thus, the scaling analysis instead uses the ratio of the Rayleigh number to the critical Rayleigh number to determine the importance of the ymomentum buoyancy term. Regardless, an analysis on the y-direction buoyancy is included in the CFD analysis.

The scaling analysis assumes constant physical properties (other than density in the buoyancy term). The variation in the three transport properties is found by varying the temperature from 310 K to 330 K and the mass fraction from 0.4 to 0.5. The difference between

the minimum and maximum transport coefficients within this range is 1% for the thermal diffusivity, 72% for the momentum diffusivity, and 57% for the solutal diffusivity. Thus, the CFD analysis assumes constant thermal conductivity and specific heat, but the mass diffusivity and momentum diffusivity (kinematic viscosity) are defined as functions of both temperature and concentration.

The focus of the CFD analysis for the heat pump, which is detailed in Appendix D, is on:

1. Heat generation in the concentration boundary layer, which will influence the temperature profile and the heat transfer coefficient.

2. Natural convection in the axial and transverse directions.

3. The effect of temperature and concentration on mass diffusivity and kinematic viscosity. Previous studies using CFD to look at flow through membrane channels have focused primarily on reverse osmosis and nano-, ultra-, and micro- filtration [148-153], membrane contactors for liquid or gas separation [154-156], pervaporation [157-160], membrane distillation [161, 162] and membrane HVAC equipment [163]. These studies looked at other terms, such as the effect of viscous heating on the temperature profile and the effect of the transverse mass flux on the velocity profile. But the scaling analysis shows that these terms are negligible for this application and thus are not considered here.

The results from the CFD analysis, which is presented in Appendix D, show that the correlations above are reasonably accurate for the geometries considered in this thesis. The model can neglect natural convection, use constant transport properties, and add the energy from the heat of mixing at the membrane surface with no effect on the results for the prototype modules. As the hydraulic diameter approaches 4 mm, the effects of natural convection and heat generation become more important.

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4.2.10 Transport coefficients: Summary

The equations for the transport coefficients are listed in Table 4.5, with all details found in the previous sections. The first two sets of equations are for the flat-sheet geometry. In summary, the coefficients for the membrane come from work on membrane distillation, the air gap coefficients are relatively simple since natural convection is found to be negligible, and the Nusselt and Sherwood numbers are modified developing-flow correlations from the heat transfer literature. The hollow fiber geometry requires modifications from the flat-sheet case, as listed at the bottom of the table. The major modifications are for the air gap, which are based on conduction shape factors and radiation view factors from the heat transfer literature.

Table 4.5: Summary of heat and mass trans	port coefficients	for the m	embrane, a	air gap,	and
boundary layers.					

Mass transport coefficients	
Membrane	$K_{\rm mem} = \frac{M_{\rm w}}{RT} \frac{1}{\delta_{\rm mem}} \frac{\varepsilon}{\tau} \left[\frac{3}{d_p} \sqrt{\frac{\pi M_{\rm w}}{8RT}} + \frac{p_{a,\rm LM}}{pD_{12}} \right]^{-1}$
Air gap	$K_{gap} = \frac{M_1}{RT} \frac{p}{p_{a,\text{LM}}} \frac{D_{12}}{d_{\text{gap,eff}}}$
Boundary layers	$Sh = 7.9 + 0.245 \exp\left(\frac{-200}{Gz_M}\right) G z_M^{\frac{1}{2}}$
Heat transport coefficients	
Membrane	$h_{\rm mem} = \frac{1}{\delta_{\rm mem}} \left(\varepsilon \lambda_{\rm g} + (1 - \varepsilon) \lambda_{\rm polymer} \right)$
Air gap ¹	$h_{\rm gap} = \frac{\lambda_{\rm g}}{d_{\rm gap,eff}} + \frac{\sigma_{\rm SB} F_{\rm 1-2}}{2/\varepsilon_{\rm rad} - 1} \left(T_{\rm 1}^2 + T_{\rm 2}^2\right) \left(T_{\rm 1} + T_{\rm 2}\right)$
Boundary layers	$Nu = 7.9 + 0.245 \exp\left(\frac{-200}{Gz_T}\right) Gz_T^{\frac{1}{2}}$
Hollow-fiber modifications	
Membrane thickness	$\delta_{\rm mem} = \frac{t \ln \frac{d_{\rm o}}{d_{\rm i}}}{\pi}$
Air gap, effective gap thickness ²	$d_{\text{gap,eff}} = \frac{2t}{a_0 \pi} \ln \left[\frac{2}{\pi} \frac{t}{d_0} \sinh \left(b_0 \frac{\pi}{2} \frac{z}{t} \right) \right]$
Air gap, view factor	$F_{1-2} = \left[1 - \left(1 - D^2\right)^{1/2} + D \tan^{-1} \left(\frac{1 - D^2}{D^2}\right)^{1/2}\right]^2 D = \frac{d_o}{t}$
Concentration boundary layer	$Sh = 4 + 0.245 \exp\left(\frac{-40}{Gz_M}\right) G z_M^{\frac{1}{2}}$
Thermal boundary layer	$Nu = 4 + 0.245 \exp\left(\frac{-40}{Gz_T}\right) Gz_T^{\frac{1}{2}}$
For flat sheets, $d_{gap,eff} = air-gap$ width Coefficients a_0 and b_0 in Table 4.2.	n. $F_{12} = 1$

CHAPTER 5 Modeling results and discussion²

This chapter presents and discusses the model results. Four designs are considered. The first two are flat-sheet, counter-flow designs; one without an air gap and one with an air gap. Results from these two designs quantify the value of the air gap. The third and fourth designs are the first generation (v.1) and second generation (v.2) hollow-fiber prototypes, which are cross-flow modules using the Oxyphan and Accurel hollow fibers, respectively.

This chapter is split into three sections. The first section focuses on the design tradeoff of selectivity vs. productivity, including an explanation of the productivity-selectivity method itself. It calculates productivity and selectivity for different air-gap widths and membrane properties. It then compares the selectivity and productivity of the four designs. The second section focuses on the flow rates. Using the finite-difference model, it considers the tradeoff between efficiency and temperature lift to find the optimal flow rates for both the water and the absorbent. The third section, combining the results from the first two sections, uses near-optimal designs and flow rates to look at the performance of the heat pump over a range of temperatures and absorbent concentrations. This section also compares the performance between the four designs and across different absorbents, and it looks at the accuracy of the analytical solution compared to the finite-difference model.

5.1 **Parametric results: Design**

The parametric analysis in this section determines how the design is affected by the airgap width and the membrane properties. This section uses the transport-coefficient equations,

² Much of the work from this chapter was published in the Journal of Membrane Science: Woods, J., J. Pellegrino, E. Kozubal, S. Slayzak, and J. Burch, Modeling of a membrane-based absorption heat pump. Journal of Membrane Science, 2009. 337(1-2): p. 113-124.

with the finite-difference model used only to estimate the polarization coefficients. When a parameter is not being varied, it is set to its baseline value (Table 5.1), unless otherwise noted. Note that the inlet temperatures of the solution and water are assumed the same. This section's focus is on design and therefore only the module parameters are being considered.

Module parameters	1		
air-gap width	d_{gap}	1	mm
porosity	3	0.7	
tortuosity factor	τ	2	
mean pore size	d_{p}	0.2	μm
membrane thickness	δ_{mem}	100	μm
channel thickness	H _{channel}	1	mm
Operating parameters			
Number of transfer units	NTU	1	
Heat capacity rate ratio	R _C	0.1	
Inlet temperatures	T _{in}	35	С
Inlet mass fraction (CaCl ₂)	ω _{in}	0.5	

Table 5.1: Baseline values for parametric analysis

5.1.1 Effect of air gap: Heat and mass transfer resistances

Figure 5.1 quantifies the effect of including an air gap. The figure shows the mass transfer resistances (left side) and heat transfer resistances (right side) for the designs with and without an air gap. By using resistances instead of transfer coefficients, the contribution of the membrane, air gap, and polarization coefficients can be directly added, as in a resistances-inseries network. Note that heat and mass transfer polarization in the boundary layers does not contribute to the overall heat transfer resistance because of the direction of the heat flows. The sensible heat 'lost' is from the point of condensation to the point of evaporation (see Figure 1.3), which is between the membrane-liquid interfaces. Convection heat transfer in the boundary

layers (polarization) moves in the opposite direction to the conductive heat transfer across the membranes and air gap.

Consider the mass transfer resistance first. Figure 5.1 shows that adding both a 1-mm air gap and an additional membrane increases the mass transfer resistance by a factor of 3 over the design with no air gap. This undesirable additional resistance is outweighed by the additional heat transfer resistance, which increases by a factor of 25. These two effects combine to increase the selectivity by a factor of 8 (\sim 25/3). As discussed in Chapter 3, the selectivity is the ratio of the latent energy transfer to the sensible energy transfer.

How does an air gap help? Consider a membrane and air gap of equal thickness. The air gap's mass transfer resistance is only 22% of that for the membrane, while the heat transfer resistance is 150% of that for the membrane. Thus, adding an air gap reduces the heat transfer coefficient more than it reduces the mass transfer coefficient, leading to a higher selectivity. But higher selectivities do not always result when increasing the air-gap width, as discussed in the next section.



Figure 5.1: Resistance of heat and mass transfer with and without an air gap (baseline membrane parameters). Including an air gap increases mass transfer resistance by a factor of 3 and heat transfer resistance by a factor of 25, improving the mass-transfer to heat-transfer ratio by a factor of 25/3.

5.1.2 Effect of the air gap width and the selectivity-productivity tradeoff

Chapter 3 introduced the tradeoff between the selectivity, corresponding to the potential temperature lift, and the productivity, corresponding to the specific heating capacity (W/m^2) . Figure 5.2 shows this relationship for both the single-membrane and air-gap designs. For the design with no air gap (the single-membrane design), making the membrane thinner increases productivity, but the selectivity remains the same. The figure shows a line for each of the thermal conductivity equations discussed in the previous chapter. Although the uncertainty in the

selectivity from these different models is near 35% for the baseline membrane, the difference between the air-gap and single-membrane designs is clear. For a productivity between 100 and $400 \text{ W/m}^2/\text{kPa}$, the selectivity of the air-gap design is at least twice that of the single-membrane design.

Focusing now on the air-gap design, notice that increasing the air-gap width reduces productivity and increases selectivity. But the selectivity increases at a diminishing rate and eventually decreases after reaching a maximum. This occurs because of the way sensible energy is transferred across the air gap. Sensible energy transfer is by conduction and radiation, while latent energy transfer (mass transfer) is by diffusion with no analogue to radiation. Radiative heat transfer is independent of the air-gap width, while conduction and diffusion are inversely proportional to this width (see Eq. 4.31). As the air gap width increases, the proportion of energy transferred by radiation increases as both conduction and diffusion become small. Eventually, increasing the air-gap width reduces mass transfer more than it reduces heat transfer and the selectivity starts to decline.

The three points on the curve in Figure 5.2 are for air gap widths of 0.5, 1, and 1.5 mm. The optimal air-gap width depends on the application, but based on the tradeoff in the figure, it is likely somewhere between 0.5 and 1.5 mm. The optimum can be determined for each application by weighting the economic value of the temperature lift versus the economic value of the desired heat flow (which is related to initial size and cost), and then minimizing the life-cycle cost. Many of the results below are based on an air-gap width of 1 mm.

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Figure 5.2: Selectivity-productivity tradeoff for designs with an air gap (air-gap design) and without (single-membrane design). Values calculated by varying air gap width for air-gap design and membrane thickness for single-membrane design. In the air-gap design, the membrane thickness is fixed at 100 μ m. Sensitivity to the membrane thermal conductivity model for the single-membrane design shown with the series (minimum conductivity) and parallel (maximum conductivity) models.

5.1.3 Effect of membrane properties

Figure 5.2 is for a specific membrane (baseline case in Table 5.1), and the lines will change if different membranes are used. This section shows the effect of membrane properties on the membrane mass transport coefficient (Figure 5.3) and then on the selectivity-productivity tradeoff (Figure 5.4). Figure 5.3 shows a range of pore sizes and three ratios of the porosity to the tortuosity factor. Increasing this ratio linearly increases the transport coefficient, while increasing pore size has a non-linear effect.

The lumped porosity-tortuosity parameter adequately captures the effect on mass transfer since porosity by itself is only important in the heat transfer coefficient. As shown in Section 4.2.2, this heat transfer coefficient has a small impact on the air-gap design. Changing porosity from 10% to 80% changes U by 6%, assuming the highest-conductivity parallel model and an air-gap width of 1 mm. In comparison, over this same porosity range, K changes by a factor of 3 (210%).

Larger pores give higher mass-transfer coefficients because Knudsen flow becomes less important and molecular diffusion becomes more important. The mass flux is linearly proportional to pore size when Knudsen flow dominates, but independent of pore size when molecular diffusion dominates. For the pore sizes and pressures considered here, both mechanisms are important and the relationship is non-linear with pore size: a steep slope for small pores where Knudsen diffusion is more important and a shallow slope for large pores where molecular diffusion is more important.

The figure is for a membrane thickness of $100 \,\mu\text{m}$, but since the transport coefficient is indirectly proportional to the membrane thickness, reducing the membrane thickness has the same effect as increasing the porosity or decreasing the tortuosity factor. Keep in mind the constraints outlined in Section 3.2.3 for pore size, porosity, tortuosity factor, and membrane thickness. These were considered in selecting the ranges for the membrane parameters in Figure 5.3.

Another constraint not yet considered is the hollow fiber inner diameter (or the channel thickness for the flat-sheet design). Smaller fiber diameters give better performance but also increase pumping energy. The smallest fibers considered here are the Oxyphan fibers, with an inner diameter of 280 µm. The pumping energy required for both the solution flow and the water

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flow is only 1% of the heat delivered by the device. This is calculated using an upper-limit viscosity for the solution flow of 0.02 kg/m-s. This is not to say that the viscosity is not important, as the pumping power to transport the solution over long distances can be significant for certain applications. But it is not considered in this analysis, which focuses only on the heat pump component. See Section 5.3.2 on absorbent properties for more on how viscosity changes with concentration and with different absorbent salts.

Although pumping energy is not important, an even smaller diameter fiber could give higher temperature lifts by reducing temperature and concentration polarization. But this polarization is only 2% of the overall mass transfer resistance for the Oxyphan fibers (see Section 6.3). So using hydraulic diameters less than around 300 µm does not significantly improve performance. And the pumping energy saved with larger hydraulic diameters is also not significant. Thus, the hydraulic diameter does not affect performance assuming the model is valid over this range of diameters. The CFD analysis in Appendix D shows that some of the assumptions break down for larger diameter fibrs. However, these sizes (greater than 4 mm) are larger than those discussed here, and the hydraulic diameter is not discussed in more detail in this Chapter.



Figure 5.3: Effect of membrane porosity-tortusoity ratio and pore size on membrane mass transport coefficient. $\delta_{mem} = 100 \ \mu m$.

Figure 5.4 shows the selectivity-productivity tradeoff for different membranes. As expected, as the membrane improves, the selectivity for the single-membrane design improves. It also plays an important role in the air-gap design, even though the air gap is the dominant heat transfer resistance. The heat and mass transfer resistances of the air gap become more dominant as the air gap width becomes larger (left side of Figure 5.4) and the three lines start to converge. Note, though, that the maximum selectivity is obtained at different productivities for the different membranes. The optimal air gap width is also different for each case. Figure 5.5 replots the data from Figure 5.4 with air-gap width on the x-axis. Although the air gap width with the maximum selectivity is not necessarily optimal, it is used here to compare the three cases in Figure 5.5. In

these three cases, the maximum selectivity occurs at 1.5, 2, and 3.7 mm for porosity/tortuosity ratios of 0.5, 0.3, and 0.1, respectively. Due to the tradeoff between productivity and selectivity, the optimal air gaps might be closer to 0.75, 1, and 2.5 mm. Thus, the optimal air-gap width will be different depending on which membrane is used.



Figure 5.4: Selectivity-Productivity plot for different membrane porosity-tortuosity ratios. $d_p = 0.2 \ \mu m$, $\delta_{mem} = 100 \ \mu m$. With air gap (---); without air gap (---).



Figure 5.5: Selectivity vs. air-gap width for different porosity-tortuosity ratios. Peak selectivity occurs at lower air-gap widths as membrane permeability increases.

5.1.4 Comparison of module designs

The design goal for the heat pump module is to increase both productivity and selectivity, and thus move towards the upper-right hand corner of the selectivity-productivity plot. Using the flat-sheet module, the optimal air-gap width is near 1 mm. This was the basis for selecting 0.5, 0.75, and 0.91 mm for the air-gap widths for the hollow-fiber module prototypes. However, the hollow fibers used in the prototype had a much lower permeability than many commercially available membranes. This lower permeability results in a different shape for the selectivity-productivity curve for the prototype module, as shown in Figure 5.6. Basing the design off of this

line, the prototypes should have perhaps used air gaps closer to 2 to 3 mm. However, due to the tradeoff with productivity, using this larger air gap would lower the vapor flux. As discussed in Chapter 6, the uncertainty in the measurements is primarily from measuring vapor transfer with scales that measure mass gains and losses from the absorbent and refrigerant tanks. Thus, further reducing this measurement response would eventually lead to unacceptable uncertainties in the mass transfer coefficient.

Figure 5.6 also plots the measured selectivity and productivity from the experimental results of Chapter 6. The three points follow the expected trend of increasing selectivity and decreasing productivity as the air gap increases. Note that the primary reason the points fall below and to the left of predicted is because the experimental data includes polarization effects, whereas the prediction does not. The prediction is simply based on series addition of the transport coefficients for the membranes and air gap (see Eq. 4.14 and 4.15 on page 67).

The next design will use the Accurel hollow fibers, which have a higher mass-transfer coefficient than the Oxyphan fibers used in the first prototype. These were not used in the first prototype due to concern over leaks through the larger-pore membranes, as discussed in Chapter 3. It is included in Figure 5.6 as the line labeled 'Hollow-fiber, v.2.' This design shows potential improvement compared to the first-generation prototype. This second generation hollow-fiber design is still below the flat-sheet design because the membranes are thicker (150 μ m) than the assumed flat sheets (100 μ m). Note, though, that the hollow-fiber design is not inherently worse than the flat sheet design.



Figure 5.6: Selectivity-productivity tradeoff for the experimental prototype (Hollow fiber, v.1), an improved, 2^{nd} -generation prototype (Hollow fiber, v.2), and a theoretical, flat-sheet design. Also shown are average experimental measurements from three of the hollow fiber, v.1 prototypes.

5.2 **Parametric results: Flow rates**

This section uses the baseline, flat-sheet design (Table 5.1) to investigate the effects of the absorbent and refrigerant flow rates on temperature lift and efficiency. Both of these metrics are defined in Section 3.3.2. That section also introduces two dimensionless numbers adapted from heat exchanger analysis to represent the absorbent and refrigerant flow rates. The first is the number of transfer units, or NTU. The second is the heat capacity rate ratio, or $R_{\rm C}$, which is the ratio of flow-weighted heat capacities of the two liquids.

Figure 5.7 shows the temperature profiles for different heat capacity rate ratios.

Increasing R_c reduces the water outlet temperature, which has two effects. First, it lowers the vapor pressure on the water side. This reduces the driving potential for vapor transfer and therefore reduces the temperature lift. Second, it increases the driving potential for sensible heat transfer, which also reduces the temperature lift. Thus, low heat capacity ratios give higher temperature lifts; the water mass flow rate should be set much higher than the solution mass flow rate. Subsequent results are for R_c values of 0.1 or 0.2. Although increasing the water flow rate increases the parasitic pumping power, implying an optimum ratio could be calculated if parasitic power were considered, this is a small effect as discussed in Section 5.1.3.



Figure 5.7: Temperature profiles for three flow-weighted heat capacity ratios. $T_{in} = 45^{\circ}$ C, NTU = 0.7. The solution enters on the left, the water on the right. Lower flow-weighted heat capacity ratios give larger solution-side temperature lifts and smaller water-side temperature lifts.

Figure 5.8 shows the temperature profiles for different values of NTU. The NTU is varied in the model with the solution flow rate. Increasing NTU means a lower solution flow rate for a given surface area, and thus gives higher temperature lifts. But since the solution flow rate is proportional to the heating capacity (kW) of the device, this also means a higher cost (more surface area) for a given temperature lift. This represents one of the tradeoffs: cost vs. temperature lift. There is a second tradeoff related to NTU. For a constant R_C, increasing NTU also means a lower water flow rate for a given surface area, and this gives a higher temperature change on the water side, which reduces efficiency. Thus, the second tradeoff is between the temperature lift and the efficiency.



Figure 5.8: Temperature profiles for three number of transfer unit (NTU) values. $T_{in} = 45^{\circ}C$, $R_C = 0.6$. The solution enters on the left, the water on the right. Higher NTUs correspond to lower flow rates, and therefore larger temperature changes.

This tradeoff between efficiency and temperature lift effectiveness is shown in Figure 5.9. Although the pumping energy affects this tradeoff, it is neglected here since it is much less than the latent energy transferred between the two liquid flows (see Section 5.1.3). As NTU increases, the ratio of latent energy transfer to the solution flow-weighted heat capacity increases (by definition), but the ratio of sensible energy transfer to this flow-weighted heat capacity also increases, reducing the efficiency. Based on Figure 5.9, there is little additional temperature lift for NTU > 1.



Figure 5.9: Tradeoff between efficiency and effectiveness. Calculated using the flat-sheet model with baseline parameters from Table 5.1 while varying the NTU.

5.3 **Parametric results: inlet temperatures and concentration**

The temperature lift is not a constant for a given design but varies as a function of temperature and absorbent concentration, as shown in Figure 5.10. Also shown is the theoretical maximum temperature lift for an inlet temperature of 35° C (Δ T_{lift,max} is weakly dependent on temperature, as discussed in Section 3.1). The effect of absorbent mass fraction is understandable: higher mass fractions give lower water activities and therefore higher temperature lifts. Thus, lower temperatures also reduce the temperature lift because the saturation concentration increases with temperature.



Figure 5.10: Temperature lift as a function of inlet temperatures and absorbent concentration, in this case CaCl₂. $\delta_{gap} = 1 \text{ mm}$, $R_C = 0.1$, NTU = 1.2. ΔT_{max} is for a water temperature of 35°C. Each line ends at the mass fraction corresponding to saturation at the inlet temperature.

Lower inlet temperatures reduce the temperature lift for another reason. Ideally, the heat for the evaporator will come from the ambient temperature, which is at the low end of the temperatures considered here. Thus, it is worth investigating further why the heat pump performs poorly at this lower temperature. Consider the selectivity equation from Section 3.3.1, which is repeated here:

$$\alpha_{\text{selectivity}} = \frac{\Delta T}{\Delta p_{v}} = \frac{KH_{v}}{U}$$
(5.1)

The last part of this equation is the calculated selectivity, which depends on the device design. The middle part is the temperature lift divided by the vapor pressure driving force. For a given design (fixed KH_v/U), higher vapor-pressure driving forces give higher temperature lifts. Now consider the non-linear vapor-pressure curves for water and the absorbent solution shown in Figure 5.11. The water activity of the solution is nearly constant and therefore the solution vapor pressure is a near-constant fraction of the water vapor pressure. Assuming a temperature lift of 10°C, the water vapor pressure at 20°C is 1.4 kPa greater than the solution vapor pressure at 30°C. But at a higher water temperature of 40°C, the water vapor pressure is 4.3 kPa greater than the solution vapor pressure at 50°C. Thus, even though the ratio of the solution vapor pressure to that of the water is constant, the delta between the two is not. And this delta is the driving force for mass transfer.

This can also be seen in the analytical solution (Eq. 3.38) in Section 3.3.4. With the assumptions made for the analytical solution, the temperature lift is proportional to $T^2 / (T^2 + constant)$. Thus, higher inlet temperatures increase the temperature lift.



Figure 5.11: Vapor pressure as a function of temperature for water and the absorbent solution. For a given 10°C temperature difference, mass-transfer driving force is much smaller at lower temperatures than high temperatures.

5.3.1 Comparison of finite-difference model and analytical solution

This is a good place to compare the analytical solution to the numerical model since the temperature and concentrations strongly affect temperature lift. Figure 5.12 shows the temperature lifts for different $CaCl_2$ mass fractions and three temperatures. The figure shows that the analytical solution becomes less accurate for higher concentrations and higher temperatures. This difference is due to the assumptions made for the analytical solution, primarily the linear approximation for the vapor pressure difference, which is more important at higher temperatures, and neglecting concentration polarization, which is more important at higher concentrations.

This justifies the need for the finite-difference model, particularly for model-experiment comparisons in the next chapter. But the analytical solution is still valuable for showing the influence of each parameter in a single equation. It can also be valuable for future sensitivity analyses, where thousands or tens of thousands of runs are required. The accuracy is sufficient enough for these purposes.



Figure 5.12: Comparison of predicted temperature lifts from analytical solution (dashed lines) and numerical model (solid lines) for CaCl₂. Maximum temperature lift is also shown for an inlet temperature of 35°C. Analytical solution deviates from numerical model at higher temperatures, where the linear approximation for the vapor pressure difference is less accurate.

5.3.2 Absorbent

Selecting the absorbent is a complex problem which this section only begins to address. There are many tradeoffs, with the most important being between the unit cost (\$/kg) and the water activity. The optimal absorbent depends on the application (e.g., how much is stored, what are the operating temperatures?). This analysis simply looks at a few important tradeoffs as a basis for future optimization studies.

As discussed in Section 3.2.1, the OLI thermodynamic framework is used to predict chemical and physical properties of absorbent salt solutions and their mixtures. The software's formulation is based on regression fits to single-component aqueous solutions and a thermodynamic framework for their mixtures. The software calculates the equilibrium in multiphase, multi-component aqueous solutions by calculating both the standard-state and excess Gibbs free energies (or chemical potentials) of each species in solution. The standard state chemical potentials are based on a theoretical equations of state developed by Helgeson et al. [164-167], while the excess properties are based on formulations for the activity coefficients from several researchers [167-172]. This framework is used to calculate each of the properties discussed in this section.

The key property for improving heat pump performance is the water activity: lower water activities result in higher mass-transfer driving forces, and therefore higher temperature lifts. Figure 5.13 shows the water activity for four pure salts and one salt mixture over a range of minimum operating temperatures. This 'minimum' temperature is for the entire system (e.g., including tanks and pipes). The system must operate above this temperature at all times to avoid the saturation line, which is shown in Figure 5.14.

The operating temperature is important for the calcium salts. At higher temperatures, CaCl₂ and CaBr₂ may be favored because of their lower cost. They are limited at lower temperature though, where saturation becomes a problem, especially for CaCl₂. Also shown in Figure 5.13 is the water activity for a mixture of LiCl and CaCl₂, with the saturation mass fractions in Figure 5.15. The LiCl-CaCl₂ salt mixture is the only one shown for two reasons.

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First, it was the only mixture that reduced the water activity relative to that of the pure salts. Second, LiCl is the best-performing salt, but is the most expensive, while $CaCl_2$ is the cheapest salt. Thus, replacing some LiCl with $CaCl_2$ results in a cost savings without degrading performance. The cost savings range from 11% at 0°C to 34% at 40°C, assuming a LiCl cost ten times higher than $CaCl_2$, which at today's prices is conservative. The total mass fraction is higher than that for either pure $CaCl_2$ or pure LiCl at each temperature. More importantly, though, the amount of LiCl is less than the pure amount of LiCl and the water activity is nearly the same as that for pure LiCl.



Figure 5.13: Water activity for various absorbents at mass fraction just below saturation. Relative mass fractions of CaCl₂ and LiCl in CaCl₂-LiCl mixture shown in Figure 5.15.



Figure 5.14: Saturation mass fraction for LiCl, CaCl₂, MgCl₂, and CaBr₂.



Figure 5.15: Saturation mass fraction for LiCl-CaCl₂ mixture. Pure LiCl and pure CaCl₂ lines shown for comparison. LiCl 'savings' is the amount of LiCl that is removed from the mixture while keeping the same water activity.

The temperature lifts provided by the LiCl-CaCl₂ mixture are shown in Figures 5.16 and 5.17 for operating temperatures of 20° C and 35° C, respectively. These two mixtures are at least 25% and 32% cheaper, respectively, than pure LiCl. Temperature lifts for the LiCl-CaCl₂ mixture are similar to those for pure LiCl, but at higher concentrations. It's particularly valuable at room-temperature (20° C), where CaCl₂ is limited by its solubility at lower temperatures.

One final property to consider is viscosity, particularly for long-distance thermal energy transport, where larger amounts of energy are needed for pumping. Figure 5.18 shows that the viscosity and water activity are inversely related and thus there is likely some optimum concentration when considering pumping energy. It also shows that using the LiCl-CaCl₂ mixture instead of pure LiCl will require more pumping energy as the viscosity for the mixture is higher than for pure LiCl.



Figure 5.16: Temperature lifts for LiCl, CaCl₂, and a LiCl-CaCl₂ mixture at 20^o C. Lines end at 1% below the solubility limit at the specified temperature. NTU = 1, $R_C = 0.2$, p = 100 kPa.



Figure 5.17: Temperature lifts for LiCl, CaCl₂, and a LiCl-CaCl₂ mixture at 35° C. Lines end at 1% below the solubility limit at the specified temperature. NTU = 1, R_C = 0.2, p = 100 kPa.



Figure 5.18: Viscosity relative to pure water vs. water activity for different LiCl-CaCl₂ mixtures. Each line represents a range of concentrations of LiCl, with the mass fraction of CaCl₂ set at 0%, 10%, 20%, or 30%.
5.4 Parametric results: module layout

Figure 5.19 plots the predicted temperature lifts from (1) the theoretical, flat-sheet model, (2) the model of the prototype module, (3) the model of the second-generation prototype using Accurel hollow fibers, and (4) the flat-sheet, single-membrane model. Neither of the hollow-fiber designs reaches the performance of the theoretical, flat-sheet design, but the higher-flux Accurel membranes come within 10%. Keep in mind that the flat-sheet model does not include the spacer in the air gap, which would most likely reduce the temperature lift.



Figure 5.19: Temperature lifts using LiCl for: theoretical, flat sheet module with a 1-mm air gap (Flat sheet, air gap) and without an air gap (Flat sheet, single membrane); validated model from this work on the module using Oxyphan fibers with $d_{gap} = 0.91$ mm (Hollow fiber, v.1); theoretical hollow fiber module using membrane properties for Membrana Accurel PP hollow fibers listed in the text (Hollow fiber v.2). NTU = 1, R_C = 0.2, p = 83 kPa (lab pressure), T_{in} = 25° C.

CHAPTER 6 Experimental analysis³

This section validates the modeling with experiments on three hollow-fiber v.1 prototypes; each prototype has a different air-gap width. The experiments were performed in Golden, Colorado where the ambient pressure is approximately 83 kPa. This chapter outlines the experimental setup, discusses the experimental results, and then compares these results with calculated results from the numerical modeling (Chapter 4).

6.1 **Experimental setup**

The experimental setup is shown in Figure 6.1. The key measurements were the liquids' flow rates, the vapor mass flux, the temperatures, and the solution's water activity.

The two liquids were pumped through the module with a dual-channel peristaltic pump (Cole-Parmer Masterflex L/S), with flow rates set by pump speed and pump-tubing inner diameter. The absorbents were aqueous solutions of either lab-grade CaCl₂ from Univar, USA or LiCl from Kathabar Systems, which also includes an anti-corrosion agent. The refrigerant was deionized water. The pump was calibrated by collecting and weighing the liquid exiting the pump over a given time period. This was done for all three liquids (LiCl, CaCl₂, and deionized water), for each tubing diameter, and for each pump speed.

The vapor mass flux is calculated by measuring the change in mass of the refrigerant and absorbent tanks over time with the tanks sitting on scales (Adam Equipment CBK). Tubing from the tanks is supported to minimize errors from changes in mass other than the amount of liquid in

³ Much of the work from this Chapter was published in the Journal of Membrane Science: Woods, J., J. Pellegrino, E. Kozubal, and J. Burch, Design and experimental characterization of a membrane-based absorption heat pump. Journal of Membrane Science. In Press, Corrected Proof. DOI: 10.1016/j.memsci.2010.11.012.

the tank. Using two tanks gives a redundant measurement for the mass flux, adding confidence to the measurement.

Temperatures at the inlet and outlet of the module are measured with PFA-coated, type-T thermocouples inserted inside the tubing. The inlet and outlet thermocouples from each stream were calibrated in a constant-temperature bath to reduce uncertainty in the differential temperature measurement. Temperature data are recorded at a 2-second sample rate with an Agilent 34970A data acquisition switch unit and Agilent 20-channel multiplexer. Two constant-temperature baths (Polyscience circulating bath and ThermoScientific refrigerating circulator) control inlet temperatures. To minimize heat loss to the ambient, the module is insulated with two-inch foam-board on all six sides and the inlet and outlet tubing is insulated with half-inch polyethylene foam insulation.

The water activity was set by the $CaCl_2$ and LiCl mass fractions, which varied from 0.3 to 0.39. It was calculated by measuring density with an accurate volumetric flask and highprecision scale, and then using two correlations from Conde [94]: one for density to mass fraction and one for mass fraction to water activity.

Variables having a potential influence over the results are shown in Table 6.1 and Table 6.2. The controlled variables, such as the specific membrane used and the module size, were the same for all test modules, while the experimental variables were varied between runs. These experimental variables, which are shown for each run in Table 6.3, were the air-gap width, which was different for each module, the inlet temperatures, the inlet water activity (species concentration), the flow rates, and the salt species that was used. In Table 6.3, the flow rates are represented by the number of transfer units (NTU) and the ratio of flow-weighted heat capacities (R_c), which are discussed in Section 3.3.2. There were a total of 23 tests, with four of these being

replicates. Thus, this is a partial factorial design focused on assessing the validity of the model and does not look at all sets of levels of the experimental variables.

The unsupervised variables are shown in Table 6.2, which include the measured response variables, the concomitant variables, which were measured but unaccounted for in the modeling, and the extraneous variables, which were unmeasured.

Controlled	Experimental
Membrane	Air gap width
transport parameters	0.56, 0.71, 0.91 mm
dimensions	Inlet concentration (by mass)
Module geometry	0.3, 0.34, 0.39
heat and mass transfer area	Salt species
number of fibers	CaCl ₂ , LiCl
Experimental setup	Solution flow rate
insulation level	0.6-1.3 g/s
thermocouple placement	Water flow rate
	0.3-3.5 g/s

Table 6.1: List of all supervised variables (controlled and experimental)

Table 6.2: List of all unsupervised variables (response, extraneous, and concomitant varialbes)

Response	Concomitant	Extraneous
Outlet solution temperature	ambient temperature	Ambient humidity
Outlet water temperature	tank internal temperatures	Ambient pressure
Mass transfer rate	water flow pressure	Ambient electro-magnetic noise
	salt solution flow pressure	
	duration of data collection	



Figure 6.1: Setup for heat pump prototype experiments. T = thermocouple, P = pressure transducer. Pressure transducers used to monitor pressure entering the module.

Test	Salt	Module #	NTU	$R_{ m C}$	a_{w}^{-1}	$T_{\rm inlet}$
1	CaCl ₂	2	1.67	0.16	0.64	22
2	CaCl ₂	2	1.28	0.16	0.65	22
3	CaCl ₂	2	1.30	0.22	0.62	22
4	CaCl ₂	3	1.31	0.22	0.63	22
5	CaCl ₂	1	1.49	0.22	0.63	22
6 ^a	CaCl ₂	1	1.02	0.21	0.64	23
7	CaCl ₂	1	0.96	0.21	0.63	24
8 ^a	CaCl ₂	1	1.04	0.21	0.63	24
9 ^a	CaCl ₂	1	1.04	0.21	0.63	24
10	LiCI	3	1.22	0.2	0.32	37
11	LiCI	3	0.53	0.2	0.31	16
12	LiCI	3	0.87	0.2	0.33	25
13 ^b	LiCI	3	0.81	2.7	0.35	26
14 ^b	LiCI	3	0.79	2.7	0.35	26
15	LiCI	3	0.63	0.81	0.28	26
16	LiCI	3	0.87	0.2	0.29	26
17	LiCI	1	0.87	0.8	0.32	26
18	LiCI	1	0.69	0.82	0.32	26
19	LiCI	1	0.95	0.2	0.33	26
20 ^{2,c}	LiCI	3	0.80	0.19	0.21	26
21 ²	LiCI	3	0.79	0.19	0.21	26
22 ^{2,c}	LiCI	3	0.79	0.19	0.21	26
23	LiCI	3	1.30	0.19	0.24	36

Table 6.3: List of experimental tests. Tests are shown in the order in which they were performed. All tests were performed at an ambient pressure of approximately 83 kPa. Results for each test are labeled with the corresponding test number in Figures 6.3 to 6.5.

¹ Water activity: $a_{\rm w} = p_{\rm v} / p_{\rm v,pure water}$.

² Tests 20, 21, and 22 were performed with the same module in succession in a horizontal, vertical, and horizontal orientation, respectively. All other tests were performed in the horizontal configuration.

^{a,b,c} Tests with the same superscript letter show replicate tests

Three parameters, discussed in Section 3.3, characterize the heat pump module: the

temperature lift (ΔT_{lift}), the overall mass transfer coefficient (*K*), and the overall heat transfer

coefficient (U). These are calculated from the supervised variables and the two response

variables. The experimental versions of the three parameters are calculated with:

$$\Delta T_{\text{lift,exp}} = T_{\text{s,out}} - T_{\text{w,in}}$$
(6.1)

$$K_{\rm exp} = \frac{J_{\rm v}}{\Delta p_{\rm vLM}} \tag{6.2}$$

$$U_{\rm exp} = \operatorname{average}\left(\frac{J_{\nu}AH_{\nu} - \dot{m}_{\rm w}c_{\rm p}\Delta T_{\rm w}}{A\Delta T_{\rm avg}}, \frac{J_{\nu}A(H_{\nu} + \Delta H_{\rm mix}) - \dot{m}_{\rm s}c_{\rm p}\Delta T_{\rm s}}{A\Delta T_{\rm avg}}\right)$$
(6.3)

where $T_{s,out}$ is the solution outlet temperature, $T_{w,in}$ the inlet water temperature, ΔT_s and ΔT_w the change in temperatures of the solution and water from the inlet to the outlet of the module, J_v the overall water-vapor mass flux (Eq. 6.4 below), and *A* the area of the module available for heat and mass transfer. In the prototype modules, the total area is 2500 cm². For simplicity, the calculations ignore the cross-flow correction factor (see [121]), which is greater than 0.99 for runs with R_C near 0.2 and greater than 0.96 for runs with R_C near 0.8.

The overall water vapor mass flux is calculated with the mass change in the absorbent and refrigerant tanks:

$$J_{v,exp} = \operatorname{average}\left(\frac{m_{s,tank}(t_{2}) - m_{s,tank}(t_{1})}{A(t_{2} - t_{1})}, \frac{m_{w,tank}(t_{2}) - m_{w,tank}(t_{1})}{A(t_{2} - t_{1})}\right)$$
(6.4)

where $m_{s,tank}$ and $m_{w,tank}$ are the masses of the solution and water tanks, measured at time t_1 and time t_2 .

Eq. (6.3) is calculated as the average sensible energy gained by the water flow and lost by the solution flow, which ideally should be the same. The definition of U_{exp} uses the average temperature difference (ΔT_{avg}), though the abnormal shape of the temperature profiles compared to ordinary heat exchangers makes the effective overall temperature difference difficult to define. The average temperature difference was found to represent this effective difference better than the log-mean difference. Regardless of these assumptions, for consistency, the comparison in Section 6.3 uses Equations (6.1-6.3) to calculate both the model and experimental values.

6.2 Experimental data and results

Figure 6.2 shows inlet and outlet temperature data from test number 12, showing a large change in the solution temperature compared to the water temperature due to a low ratio of flow-weighted heat capacities (R_C) of 0.2. The transport coefficients and temperature lifts are calculated with at least 300 data points (10 minutes) collected after reaching steady state, in this case starting at 18 minutes.



Figure 6.2: Inlet and outlet temperatures from the module during test # 12. T_s = solution temperature, T_w = water temperature.

Statistics for the mass and energy balances for all runs are shown in Table 6.4. The mass balance is defined as the ratio of the mass change of the solution tank to the mass change of the water tank. The energy balance is defined as the ratio of the energy entering the module to the energy exiting the module:

Energy Balance =
$$\frac{\dot{m}_{s,in}c_{p,s}T_{s,in} + \dot{m}_{w,in}c_{p,w}T_{w,in} + J_{v}A\Delta H_{mix}}{\dot{m}_{s,out}c_{p,s}T_{s,out} + \dot{m}_{w,out}c_{p,w}T_{w,out}}$$
(6.5)

As defined, an energy balance greater than one means more energy is going in than is coming out, and therefore there are heat losses to the ambient. An energy balance less than one means more energy is going out than is coming in, which is only possible due to uncertainties in the measurements. The last term in the numerator is the heat being released from the heat of mixing, which is included to be correct, but it is less than 1% of the summation in the numerator. In other words, the heat being generated is less than 1% of the energy entering the device.

The mass balances were closer to one for tests using LiCl than for tests using CaCl₂ since LiCl is a stronger desiccant and therefore had a larger signal-to-noise ratio. The 'noise' here is from any drift in the scales due to temperature changes or shifting tubing. The energy balance for both salts shows good agreement due to lower uncertainties in flow rate and temperature measurements.

Table 6.4: Statistics for mass and energy balances from experimental tests.

	mean	maximum	minimum	standard deviation
mass balance	1.001	1.31	0.75	0.128
energy balance	1.000	1.02	0.961	0.011

6.3 **Comparison of experiments and modeling**

This section compares the experimentally-measured and model-predicted values for the overall mass transfer coefficient (K), the overall heat transfer coefficient (U), and the temperature lift (ΔT_{lift}). It is split into three sections. The first section presents plots comparing the experimentally measured values with the model-predicted values. This section also discusses discrepancies between these two values and suggests potential reasons for these discrepancies.

The second section adjusts the model to account for the main reason for these discrepancies: heat losses from the experimental setup. This affects the measurement of both the overall heat transfer coefficient and the temperature lift. A second set of plots for these two coefficients compares the predicted values from this adjusted model with the experiments.

The final section discusses the adequacy of the model to predict the membrane heat pump performance for these prototypes, future prototypes, and larger-scale modules.

6.3.1 Model-experiment comparison

The plots in Figures 6.3 to 6.5 show the model-predicted and experimentally-measured values for the three response variables. A 45° line gives a visual comparison between the model and experimental values. Each data point is labeled corresponding to the test number in Table 6.3. To keep the plots readable, they exclude uncertainty bars except for a single point, and list average uncertainties in Table 6.5. Note that the experimental uncertainties for CaCl₂ are different than LiCl, as the reduced mass flux for CaCl₂ gives larger uncertainties in the vapor flux due to the resolution of the scales. This uncertainty is carried through to both the overall mass and heat transfer coefficients. The temperature lift measurement (Eq. 6.1) is not affected by the vapor flux, and therefore the uncertainty is the same for both CaCl₂ and LiCl. Also shown in Table 6.5 are the uncertainties in the modeling, which correspond to the horizontal uncertainty bars in Figures 6.3 to 6.5. These are due to uncertainties in the measured membrane properties (ϵ , τ , d_i, d_o), the air-gap width, and the Nusselt and Sherwood number correlations. The details of the uncertainty analysis are in Appendix E.

	Experimental, CaCl ₂	Experimental, LiCl	Model
Uncertainty, K $(10^6 \text{ kg m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1})$	± 2.8	± 1.2	± 1.7
Uncertainty, U (W m ⁻² K ⁻¹)	± 9	± 6	± 3
Uncertainty, ΔT_{lift} (K)	± 0.1	± 0.1	± 0.5

Table 6.5: Average experimental and model uncertainties applicable to Figures 6.3 to 6.5.

Two statistical methods measure the adequacy of the model to predict the experimental data. The first method simply calculates the coefficient of determination (an R^2 value) by using the 45° 'model' line as a regression line to the experimental data. The second method uses a goodness-of-fit test with an F-statistic comparing the residual between the model and the experimental points with the variation from one experiment to the next. In other words, it compares the lack of fit of the experimental data to a best fit line with the lack of fit of the experimental data to the model-predicted line.

This second method first calculates the sum of the square of the residuals between the model and the experimental data, called the sum-of-squares of the errors (SSE):

$$SSE = \sum_{j=1}^{N} \left(Y - \hat{Y} \right)^2$$
 (6.6)

where Y is the overall heat transfer coefficient, mass transfer coefficient, or temperature lift, and \hat{Y} is that value predicted by the model. It then calculates the sum of the square of the errors between the experimental values and a linear-regression line to the data (this line is shown below in Figures 6.3 to 6.5), called the sum-of-squares of the pure error:

$$SSPE = \sum_{j=1}^{N} \left(Y - \overline{Y} \right)^2$$
(6.7)

where \overline{Y} is the value predicted by the linear-regression model. The difference between SSPE and SSE is the sum-of-squares error due to lack of fit (SSLFE):

$$SSLFE = SSE - SSPE \tag{6.8}$$

This lack of fit error is then compared to the pure error from variation in the experiments to calculate an F statistic:

$$F = \frac{SSLFE}{SSPE}$$
(6.9)

Note that the degrees of freedom, which are normally included in this equation, were not included here since they are the same for both the experiment and the model (N - 2 = 21) and thus cancel out. The calculated F statistic is compared to the F distribution for 21 degrees of freedom to determine the confidence level (α) for which the model matches the experiments. This confidence level is the statistical probability that the model-predicted values and the experimental values are from the same distribution.

Overall mass transfer coefficient (K)

Figure 6.3 shows the model-experiment comparison for the overall mass transport coefficient, K. The figure shows good agreement between the model and the experiment, with the model matching the data with 98% confidence. The R² values (0.42 for all runs, 0.61 for LiCl runs) are lower because of the limited range of values tested (35 to 42 x 10⁻⁶ kg m⁻² s⁻¹ kPa⁻¹). This limited range is due to the small influence of the parameters varied in this study (air-gap width, temperature, concentration, flow rate). Based on results from the modeling (Chapter 4), the resistance of the two membranes, the air gap, and the convection from the bulk flow to the membrane surface account for, respectively, 87%, 11%, and 2% of the overall mass transfer resistance for the small-air-gap module and 82%, 16%, and 2% for the large-air-gap module.

Since only the Oxyphan membrane has been studied to this point, the different values of K are a result of the different air gap widths. In many membrane-distillation studies, the flow rates influence the flux and therefore K, but in this study the small-diameter fibers reduce this effect. In addition, the flow rates are limited to a range such that 0.5 < NTU < 2, with values outside this range resulting in poor heat-pump performance. This can also be seen in Figure 5.6, where the selectivity-productivity line is steep. In other words, increasing the air gap width has a small effect on productivity, with a larger effect on the selectivity.



Figure 6.3: Model-experimental comparison for overall mass transfer coefficient K. $R^2 = 0.42$, $R^2 = 0.61$ considering only LiCl tests. Confidence level from F-test, $\alpha = 0.979$.

Even though the range of K values tested is limited, and all model and experimental points match within uncertainties, there appears to be a slight bias towards a higher mass transfer

rate than that predicted by the model. Four possible explanations were considered: thermal diffusion across the air gap, a bias in the temperature measurement due to heat losses, a bias from the measurement of the membrane's pore size, and a bias in the salt solution vapor pressure correlation.

The first possible explanation is that some other transport mechanism is contributing to transport across the membrane or air gap, such as pressure diffusion, thermal diffusion, or surface diffusion through the membrane. The largest possible contribution not included in the model was the thermal diffusion, but calculating this reveals that it is less than 0.05% of the total flux.

The second possible explanation is that heat losses from the inlet and outlet tubing change the log-mean vapor pressure difference used in Eq. (6.2). This was also found to have a negligible effect on the mass transfer measurement, but the heat losses were not negligible for the heat transfer coefficient, as discussed in the next section.

The third possible explanation is that the membrane measurement process was biased in some way. However, as it turns out, this bias would make the model *overpredict* the flux, which is the opposite of what is observed. Pore size distribution influences viscous and Knudsen flux, which are present in the gas-permeation test, more than the Knudsen-molecular diffusion present in the heat pump. Thus, the measured *effective* pore size from the gas permeation test, which is used in the modeling, is higher than the actual *effective* pore size for the diffusion present in the membranes in the experiments. This would make the model overpredict the mass flux, which does not address the discrepancy in Figure 6.3. Note, though, that this effect from pore size distribution effects on gas permeation and Knudsen-molecular diffusion, see Appendix A.

The final and most likely cause for the bias in Figure 6.3 is from the measurement for vapor pressure of the salt solution. Keep in mind that this measurement is based on measuring density, which is used to infer concentration with a correlation, which is then used to infer the vapor pressure with a second correlation. The uncertainty in the measurement is a random uncertainty, but the correlations could also introduce a bias error. For example, the correlations used in this work are from empirical fits from Conde [94], but a correlation for CaCl₂ from Bui et al. [173] predicts water activities 0.5% lower than Conde's correlation. Even this small difference reduces the calculated experimental mass transfer coefficient by 1.5%, which is near the average bias seen in Figure 6.3 (1.6%). Similarly, for LiCl, the OLI software, which is a theory-based correlation, predicts lower vapor pressures (up to 3% lower) than the Conde correlations, which are simply empirical-fit correlations. This difference would change the calculated experimental mass transfer coefficients by up to 5%. In other words, the calculation of the mass transfer coefficient is very sensitive to the estimate of the water activity of the solution, which is difficult to include in a straightforward correlation. This could potentially explain the small difference between the modeled and experimentally measured mass transfer coefficients.

Overall heat transfer coefficient (U)

For the overall heat-transfer coefficient (Figure 6.4) the range of tested values is larger than for the mass-transfer coefficient since the air-gap accounts for 95% of the overall heat transfer resistance. In general, the model slightly underpredicts the actual U-values, likely due to heat lost through the module frame. The confidence level for equivalence between the model and the experiments is only $\alpha = 2.4\%$ and the R² value for the model fit is 0.7.

Heat losses increase the U-value in two ways. Consider the numerator in the second half (the solution side) of Eq. (6.3). Heat losses will reduce the measured outlet solution temperature,

which is measured slightly downstream of the module, to a temperature below the temperature at the immediate exit of the membrane exchange area. This will reduce ΔT_s and increase the calculated value of U. The second way heat losses increase the U value is seen by considering the denominator of Eq. (6.3). Since the measured outlet solution temperature is less than the temperature at the exit of the immediate membrane area, the calculated temperature difference (ΔT_{avg}) is smaller than the actual temperature difference between the solution and water in the membrane module, which gives a higher measured U value.



Figure 6.4: Model-experimental comparison for overall heat transfer coefficient U. $R^2 = 0.7$. Confidence level from F-test, $\alpha = 0.024$.

An experiment was run to test this heat loss hypothesis. The inlet and outlet insulated tubes were connected together (i.e., the module was removed) and the heat loss was measured

with the solution and water entering at 37°C. The heat loss was approximately 3 W, which is on the order of 10% of the conductive heat transfer between the solution and water inside the module during heat pump experiments. Referring again to Figure 6.4, test runs 10 and 23 are the tests with the two largest differences between the experimental and modeled U values. And these two tests were the tests run with the highest inlet temperatures. Also, note that the CaCl₂ tests (dark points) also give high values of U. Between these tests and the LiCl tests, the thermocouples were re-installed into the inlet and outlet tubing and were placed closer to the module inlets and outlets. This could explain the high values of U for the CaCl₂ tests. Most of the remaining LiCl tests appear to be more in line with the model than runs 10 and 23 and the CaCl₂ runs.

The heat losses are backed out with a calculation based on the heat loss experiment discussed in the previous paragraph. The model is compared again to this adjusted data in Section 6.3.2. Although these heat losses explain the differences between the model and experiments, keep in mind that heat losses are real in any design. Heat losses external to the module become less important as the size of the device increases, but heat losses internal to the module, between the two inlet and outlet flows, are always important and thus the design of the heat pump headers is crucial. This is one reason for using a cross-flow configuration, minimizing thermal interaction between the inlet and outlet headers of the two flows.

Temperature lift (ΔT_{lift})

The temperature lift (Figure 6.5) is affected by K and U (and therefore air-gap width) but is also strongly dependent on inlet temperatures, water activity, and flow rate. Temperature lift is higher for: higher salt concentration, higher inlet temperatures, lower solution flow rates (higher NTU) and higher water flow rates (lower R_c). The model and experimental results begin to diverge as the temperature lift increases, likely because of increased heat losses at elevated temperatures, as discussed in the previous section on the heat transfer coefficient. Because of this, the model matches this data with only 1% confidence, although the R² value of 0.91 is higher than for K and U because of the large range in values tested ($2 < \Delta T_{lift} < 10$).



Figure 6.5: Model-experimental comparison for temperature lift. $R^2 = 0.96$. Confidence level from F-test, $\alpha = 0.01$.

To investigate the effects of natural convection in the air gap, test numbers 20 through 22 (Table 6.3) are run at the same operating conditions with the module oriented horizontally, vertically, and then repeated horizontally. The transport coefficients for all three cases were within 3% and the temperature lift within 1%. Thus orientation does not have a noticeable effect

on this module's performance, reinforcing the theoretically-reinforced assumption of negligible natural convection for the dimensions considered here.

6.3.2 Comparison of model with adjusted experimental data

This section replots the model-experiment comparison for the overall heat transfer coefficient and the temperature lift after including the effects of heat losses from the module. As explained in Section 6.3.1, the heat losses were measured with an experiment using only the inlet and outlet tubing. An overall heat loss coefficient ($U_{loss}A_{tubing}$) was calculated based on these runs to be 0.2 W/K. This was used to calculate the temperatures at the immediate inlet and outlet of the module based on the measured thermocouple temperatures. These new temperatures were then used to calculate adjusted values of the overall heat transfer coefficient (U) and the temperature lift (ΔT_{lift}). The effect on the overall mass transfer coefficient is negligible.

Figure 6.6 shows this new plot for the overall heat transfer coefficient. There is still a slight bias for the model to underpredict the heat losses, but the agreement is much better after accounting for the heat losses. The model agrees with this data with 67% confidence. Figure 6.7 shows that for the temperature lift, the model matches the adjusted data with over 99% confidence. These two plots show that not accounting for heat losses for these small-scale prototypes leads to errors.



Figure 6.6: Model-experimental comparison for overall heat transfer coefficient with the data adjusted to account for heat losses. $R^2 = 0.9$. Confidence level from F-test, $\alpha = 0.67$.



Figure 6.7: Model-experimental comparison for temperature lift with the data adjusted to account for heat losses. $R^2 = 0.96$. Confidence level from F-test, $\alpha = 0.9999$.

6.3.3 Applicability of the model

The numerical model from Chapter 4, once corrected for heat losses, predicts the experimental data well. It predicts the overall mass transfer coefficient with a confidence of 98%, the overall heat transfer coefficient with a confidence of 67%, and the overall temperature lift with a confidence over 99%. Thus, for this prototype design, the model is appropriate for predicting performance within the range of parameters investigated here: Inlet temperatures between 15 and 35°C, salt-solution water activities from 0.2 to 0.65, air-gap widths from 0.56 to 0.91 mm, and over the entire range of practical flow rates. However, one should use caution when applying this model to other designs. In particular, the experiment used only a single

membrane. It is reasonable to use this model with other membranes, but scaling analyses similar to those reported in Chapter 4 should be used to increase the confidence in the model prediction.

The inherent scalability of membrane devices means the model is still applicable for larger systems. In fact, the heat losses that caused problems for testing these modules would be less important as the ratio of heat-loss-related surface area to volume decreases as module size increases. Also related to scale-up, there are some issues with increasing the dimensions within the device. In particular, it would be inappropriate to use the model to predict the performance of modules with air gaps larger than around 5 mm. As discussed in Section 4.2.7, significant natural convection can occur for these dimensions. Also, as the salt-solution channel size gets larger than 2 or 3 mm, there is a possibility for natural convection to develop in the salt-solution flow. Air gaps and channels of this size would likely not be used, as they reduce performance compared to smaller dimensions. However, larger-scale modules may require larger channels to limit the pressure drop due to friction.

CHAPTER 7 Conclusions

An absorption heat pump that operates at ambient pressure can be used in thermal energy storage and transport processes, with ambient-pressure components lowering complexity and cost. The goal of this thesis was to design, model, and test an ambient-pressure absorption heat pump. A theory on absorption heat pumps operating at ambient temperature has not been developed prior to this thesis. The science and engineering contributions of this thesis are summarized as follows: (1) design characterization of this novel device and process, with a focus on controlling the heat and mass transfer in a membrane device for unique energy storage and transport applications, (2) modeling the process, including detailed analyses of the transport phenomena and a generalized analysis of membrane pore size distribution, which is applicable to a wide range of membrane processes, and (3) experimental characterization of this process, with a validation of the model.

For the design, new hollow-fiber membrane modules were built to be used as the evaporator-absorber component in an absorption heat pump. New methods to characterize the heat pump were developed from membrane technology, heat exchanger design, and heat pump design.

There are three important modeling tasks: estimating the absorbent properties, calculating the temperature and concentrations at each point along the flows, and estimating the transport coefficients between the flows. Theoretical and data regression correlations estimate the absorbent properties, a finite difference model estimates the conditions along the flow, and detailed analyses of the transport phenomena are used as inputs into the finite difference model. Several conclusions can be drawn from the modeling results, relating to optimizing a membrane heat pump. Although a completely optimized design depends on the application and inclusion of economic weighting factors, this study developed four general design guidelines.

First, the air gap is important. It improves temperature lift and efficiency by up to 3-5 times. The space between alternating rows of hollow fibers works successfully as an air gap without the need for a support in the air gap.

Second, a limited study on absorbents showed that less expensive absorbents can be substituted for expensive absorbents with similar performance. However, the extent of this tradeoff is small. The amount of the expensive desiccant that is required decreases by 10% for a 0° C operating temperature and 33% for a 25°C operating temperature.

Third, performance of the heat pump is inherently poor at low temperatures due to the non-linear vapor pressure curve for water. The shallower slope of the p_v -T curve at low temperatures provides a lower vapor flux for a given temperature difference than the steep slope does at higher temperatures.

Fourth, there are two key tradeoffs to keep in mind. The first is the design tradeoff of productivity vs. selectivity, which is a tradeoff between the initial size and cost of the device and the device's performance. This 'performance' is the temperature lift and the efficiency. The second tradeoff between the temperature lift and the efficiency and is related to the flow rates. Reducing the flow rate of the absorbent solution increases the temperature lift but decreases the efficiency.

Additional detailed analyses of the transport phenomena, using scaling analyses and finite-volume models, led to the following conclusions:

(1) Natural convection is negligible in the air gap region between the rows of fibers.

- (2) Equations using only porosity, tortuosity factor, and pore size adequately predict membrane mass transport coefficients, particularly for this application where the air gap is a significant portion of the mass-transfer resistance.
- (3) Although many membrane researchers use the parallel thermal conductivity model, this will likely overpredict the conductivity. The geometric-mean model appears more reliable. Regardless, the choice of the thermal conductivity model is unimportant for a membrane heat pump, where the air gap dominates the overall heat transfer resistance.
- (4) Using modified developing-flow Nusselt and Sherwood number correlations, similar to the developing flow correlations from the heat transfer literature, adequately predict the internal convection coefficients, without requiring any additional consideration of the complex boundary-layer flow phenomena (e.g., mass flux at the wall).

The experiments performed on several prototypes validated these findings and the modeling approach.

Future work building upon this thesis could address three design-related issues. First, it is difficult to scale up the prototype modules from this thesis. Future work could build and model the shell-and-tube module using two bundles of hollow fibers, which is easier to scale up. The model would need to include a stochastic approach to modeling the varying air-gap width between the two sets of hollow fibers. The second design modification would be to use flat-sheet membranes with a low-conductivity spacer in the air gap. Although this would not, in general, perform better than the current hollow-fiber design, it is a better starting point for a staged design, which could significantly increase the temperature lift. The third design modification

would be to use an air-based system, where the water vapor is coming from a saturated air flow rather than a liquid water flow. This design would be better integrated into an air-based HVAC system where building exhaust air could be used for the water source. There are many engineering issues to address with these alternative designs, but all of them have the potential to improve some aspect of a membrane heat pump.

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Appendix A

Pore-size distribution analysis for membrane distillation⁴

A.1 Introduction

The work in this appendix expands on the assumption in Chapter 4 that the membrane's pore-size distribution has only a minimal impact on the performance of a membrane heat pump. The focus of this appendix is on membrane distillation, a process similar to a membrane heat pump. Membrane distillation (MD) is a separation method where a non-wetting, macroporous membrane (e.g., a microfiltration membrane) is used with a liquid feed phase on one side and a condensing, permeate phase on the other. Here, thermal energy creates a vapor-pressure driving force and removes the most volatile component from the feed phase. Commonly this is water in a desalination process. Membrane distillation creates concentrated and diluted streams using temperature gradients, whereas the membrane heat pump creates temperature gradients using concentrated and diluted streams. The following discusses the effects of pore size distribution on both of these processes; initially focusing on MD and then extending the analysis to a membrane heat pump. As discussed in Chapter 3, the error in neglecting pore size distribution is likely less than 1% in predicting temperature lift in a membrane heat pump.

⁴ The work in this appendix was published in the Journal of Membrane Science: Woods, J., J. Pellegrino, and J. Burch, Generalized guidance for considering pore-size distribution in membrane distillation. Journal of Membrane Science, 2011. 368(1-2): p. 124-133.

A.2 Background

In 2006, El-Bourawi et al. [14] noted that pore-size distribution was considered in very few models in MD research, despite the dominant role that they suggested it may play in the future of MD. Prior to 2006, some MD studies [114, 115, 174-176] looked at pore-size distribution, but their analyses were either brief or focused only on the particular membrane they were studying. An extensive literature search found no papers since 2006 addressing in any detail the effects of pore-size distribution on MD flux.

The purpose of this appendix is to determine how pore-size distribution affects directcontact, vacuum, and air-gap MD and to provide guidance to MD modelers on when a singlepore-size model is adequate and when a more rigorous pore-size-distribution analysis is needed. Note that the paper does not address the effects of pore size distribution on selectivity, as a very large pore size distribution will obviously lead to pore breakthrough and will allow solutes to pass through the membrane.

The paper is outlined as follows. Section A.3.1 presents the chosen transport model: common pore-transport equations from the MD literature. Section A.3.2 presents the model for considering all the pores in a pore-size distribution. This model, similar to those of of Lagana et al. [174] and Martinez et al. [175], is compared to other pore-size distribution models in the MD literature [114, 115, 176-178] in Section A.3.3. Section A.3.4 summarizes the analysis methods for gauging the effect of neglecting pore-size distribution in MD, with the results presented in Section A.4.1. To gauge its importance, the effect of neglecting pore size distribution is compared to: (1) experimental results and uncertainties from the MD literature (Section A.4.2), and (2) the effect of neglecting pore-size distribution in other membrane processes (Section A.4.3). Section A.4.4 then presents the errors in assuming a single pore size when modeling direct-contact, air-gap, and vacuum MD transport coefficients.

In general, the analysis presented herein can be considered appropriate for assessing the influence of pore size distribution on any transport scenario for which the presented assumptions are appropriate. Thus, a secondary motivation for this work is to determine the effect of pore-size distribution on the performance of a membrane heat pump (Section A.4.5), whose transport phenomena are congruent with direct-contact MD. A membrane heat pump consists of an aqueous low-activity solution flow separated from a water flow by a vapor-permeable membrane. The low activity of the solution results in a net flux of water vapor across the membrane, which heats the solution flow and cools the water flow, creating a temperature lift. This example also shows how other factors (e.g., polarization) can reduce the effects of pore size distribution.

A.2.1 Membranes for membrane distillation

Membrane distillation requires porous, hydrophobic membranes. Here the focus is on flat-sheet membranes, but the analysis is general and the conclusions are applicable to both flatsheet and hollow-fiber formats. The specifications in Table A.1 are for four commercial membranes considered by many experimentalists in small-scale MD tests, although they have not been used in larger-scale MD modules. As part of the analysis, modeled results are compared with experimental data from the literature for these membranes. The membrane specifications and their uncertainties are from typical values from the literature.

Table A.1: Specifications of membranes used in MD experiments from the literature. Geometric mean pore size (μ_a), porosity (ε), membrane thickness (δ_{mem}), and tortuosity factor (τ) from [115, 131, 136, 175, 176, 179, 180] and geometric (σ_g) and arithmetic (σ_a) standard deviations from [176, 181], [182-185].

	Manufacturer	Material	$\mu_{\rm g}$ (µm)	З	$\delta_{\rm mem}$ (μ m)	τ	$\sigma_{ m g}$	$\sigma_a (\mu m)$
GVHP	Millipore	PVDF	0.22	0.70±0.03	120±10	2 ± 0.2	1.2	0.041
HVHP	Millipore	PVDF	0.45	0.70±0.03	120±10	2 ± 0.2	1.2	0.084
TF-200	Pall-Gelman	PTFE	0.20	0.80±0.03	60±5	1.5 ± 0.2	1.1	0.019
TF-450	Pall-Gelman	PTFE	0.45	0.80±0.03	60±5	1.5 ± 0.2	1.1	0.043

A.2.2 Measuring and characterizing pore-size distributions

Before using a pore-size distribution, a research must know how the distribution was measured and the physical nature of the descriptors being used to represent it. Most researchers found their data to fit the log-normal distribution best [186-188], although some instead use a normal distribution [181, 189, 190]. The probability density function for the normal distribution is:

$$f_i = \frac{1}{\sqrt{2\pi\sigma_a}} \exp\left[-\frac{\left(d_{p,i} - \mu_a\right)^2}{2\sigma_a^2}\right]$$
(A.1)

where μ_a is the arithmetic mean, σ_a the arithmetic standard deviation, and $d_{p,i}$ the characteristic value of the pore size for the *i*th pore size interval. The log-normal distribution is:

$$f_i = \frac{1}{d_{\mathrm{p,i}}\sqrt{2\pi}\ln\sigma_g} \exp\left[-\frac{\left(\ln d_{\mathrm{p,i}} - \ln\mu_g\right)^2}{2\left(\ln\sigma_g\right)^2}\right]$$
(A.2)

where μ_g is the geometric mean and σ_g the geometric standard deviation. This work uses the geometric mean and geometric standard deviation when reporting values for the log-normal distribution. The geometric standard deviation is a measure of the variance of the distribution. One standard deviation from the mean in each direction is represented by $\mu_g \times \sigma_g$, where \times represents 'multiplied or divided by' (analogous to \pm for the normal distribution). As an example,

for a membrane with $\mu_g = 0.2$ and $\sigma_g = 1.2$, 68% of the pores (1 standard deviation) are between 0.167 and 0.24 (0.2/1.2 and 0.2 × 1.2), and 95% of the pores (2 standard deviations) are between 0.14 and 0.29 (0.2/1.2² and 0.2 × 1.2²). This analysis assumes a range of geometric standard deviations from 1 to 2. For $\sigma_g = 1$, all pores are the same size with a diameter of μ_g (the single-pore-size model). For $\sigma_g = 2$, the two-standard-deviation range is $\mu_g/4$ to $4\mu_g$. The analysis is conservative, as $\sigma_g = 2$ is larger than those measured for the membranes in Figure A.2 ($\sigma_g < 1.7$), and much larger than most commercially available membranes, where σ_g is commonly less than 1.2. For more details on the log-normal distribution and its different forms for the mean and standard deviation, see Zydney et al. [191].

Figs. 1 and 2 compare the geometric mean pore size (μ_g) and geometric standard deviation (σ_g) reported for the membranes shown in Table A.1. Different measurement techniques can lead to different mean pore sizes and standard deviations due to instrumental and mechanism-related biases. This paper lists the reported measurements from the following methods: atomic-force microscopy (AFM), scanning-electron microscopy (SEM), gas permeation, liquid displacement, and mercury intrusion, with minimal critique. Details on these techniques can be found elsewhere [188, 192, 193]. Although the measured pore size data can be used directly in modeling, the measured data is often fit to a log-normal distribution defined by μ_g and σ_g . It is generally not known specifically what the manufacturers report for the pore size (is it the most likely value, or μ_a or μ_g ?), but the results in Figure A.1 suggest that they are reasonably consistent with μ_g found by the investigators, except for AFM data. The higher readings from AFM are consistent with the findings of Khulbe et al. [193]. Figure A.2 suggests that AFM may also give high values for σ_g .



Figure A.1: Measured geometric mean pore size (μ_g) from various methods and the mean pore size specified by the manufacturer. SEM: scanning electron microscopy, AFM: atomic force microscopy. Data from [115, 176, 181], [182-185].



Figure A.2: Geometric standard deviations from the literature measured by various methods. Data taken from [176, 181], [182-185].

A.3 Modeling

A.3.1 Pore-transport model

The dusty-gas model [125] is used for calculating the vapor flux through each pore size in a distribution, as is often done in the MD literature [17]. Assuming negligible thermal, pressure, and surface diffusion, this work's model adaptation considers three transport mechanisms: Knudsen or free-molecular flow, viscous flow, and molecular or ordinary diffusion. The relative importance of these mechanisms depends on the size of the pore, the temperature and pressure, and the type of gradients present (vapor concentration vs. total pressure). The dependence on pore size, temperature, and pressure can be expressed with the dimensionless Knudsen number, which is the ratio of the mean free path (λ) of the transported molecules to the pore diameter (d_p):

$$Kn = \frac{\lambda}{d_{\rm p}} \tag{A.3}$$

For direct-contact MD, assuming constant total pressure in the membrane pores and negligible air flux, results in the familiar Bosanquet equation [126] for the vapor mass flux:

$$n_{1} = -\frac{M_{1}}{RT} \left[\frac{1}{D_{K}} + \frac{y_{2}}{D_{M}} \right]^{-1} \nabla p_{1}$$
(A.4)

where $D_{\rm M}$ and $D_{\rm K}$ are the molecular-diffusion and Knudsen-flow transport coefficients for water vapor, y_2 the mole fraction of air, p_1 the partial pressure of water vapor, M_1 the molecular mass of water, T temperature, and R the universal gas constant.

Assuming cylindrical pores, the molecular-diffusion and Knudsen-flow transport coefficients for water vapor (species 1) are:

$$D_{\rm M} = \frac{\varepsilon}{\tau} D_{12} \tag{A.5}$$

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$$D_{\rm K} = \frac{\varepsilon}{\tau} \frac{d_p}{3} \sqrt{\frac{8RT}{\pi M_1}}$$
(A.6)

where ε is the porosity and D_{12} the binary diffusion coefficient for water in air. As is often done in the MD literature, the equation assumes that the deviation of pores from being straight, cylindrical, and non-interconnected is effectively captured in the tortuosity factor (τ). The combined transport coefficient for direct-contact MD is:

$$D_{\mathrm{K}-\mathrm{M}} = \left[\frac{1}{D_{\mathrm{K}}} + \frac{y_2}{D_{\mathrm{M}}}\right]^{-1} \tag{A.7}$$

For air-gap MD (and the membrane heat pump in Section A.4.5) the analysis uses Eq. (A.7) for the membrane transport coefficients and then add a resistance for the air gap (cf. Eq. A.19).

For vacuum MD, the analysis assumes only water vapor is present, and thus there is no molecular diffusion. This leads to Knudsen and viscous resistances in parallel:

$$n_1 = -\frac{M_1}{RT} \left[D_{\rm K} + \frac{\kappa \, p}{\eta} \right] \nabla p \,. \tag{A.8}$$

where κ is the Darcy's Law permeability, *p* the total pressure, and η the dynamic viscosity. A combined transport coefficient for vacuum MD can be defined as:

$$D_{\rm K-V} = D_{\rm K} + D_{\rm V} \tag{A.9}$$

where, although viscous flow is not diffusion, the lumped permeability coefficient for viscous flow ($\kappa p/\eta$) is replaced with the letter *D* to be consistent with the coefficients for molecular diffusion and Knudsen flow, and because it has the same units as diffusivity (m² s⁻¹). Assuming straight, cylindrical, non-interconnected pores corrected by a tortuosity factor, this viscous transport coefficient is:

$$D_{\rm V} = \frac{\kappa p}{\eta} = \frac{\varepsilon}{\tau} \frac{d_{\rm p}^2 p}{32\eta} \tag{A.10}$$

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Eq. (A.9) is often referred to as the transition-flow transport equation with the first term representing slip flow. Many modifications of this simple addition of viscous and Knudsen flow exist, as discussed by Hernandez et al. [189]. In this work there are no empirical correction factors, with some of the other possible formulations discussed in Section A.3.3.

The two combined-transport coefficients (D_{K-M} , D_{K-V}) are the ones of interest, with the other coefficients (D_V , D_K , D_M) representing their asymptotic values. Figure A.3 shows the dependence of these transport coefficients (solid lines) and asymptotes (dashed lines) on the Knudsen number (and implicitly the pore size) for p = 100 kPa, T = 25°C, and saturated air. For vacuum MD, the average pressure is on the order of 1 kPa and the Knudsen number is 1-2 orders of magnitude higher for a given pore size. This is clarified in Section A.3.3 when looking specifically at vacuum MD (cf. Figure A.4).

The Knudsen number on the x-axis in Figure A.3, and in subsequent plots, is varied by changing the pore size at a specific pressure and temperature, because this work looks at how the transport coefficient changes for different pore sizes in the distribution, while the temperature and pressure are relatively constant from one pore to the next. If the Knudsen number is varied by changing pressure or temperature instead, the shapes of the lines in Figure A.3 would be different. This is discussed further in Section A.4.1.



Figure A.3: Membrane transport coefficients vs. Knudsen number. Calculated for water vapor transport with p = 100 kPa, $T = 25^{\circ}$ C, $p_1 = 3.14$ kPa (water saturation pressure at 25°C), $\varepsilon = 0.7$, $\tau = 2$, and $\eta = 9.87 \times 10^{-6}$ kg m⁻¹ s⁻¹. Note that $D_{\rm M}/y_2$ as opposed to $D_{\rm M}$ is plotted here to compare the two terms in Eq. (A.7).

Note that each of the pore-transport equations can be represented by an equation of the form:

 $D_{\rm eff} = C_1 d_{\rm p}^m = C_2 {\rm Kn}^{-m}$ (A.11)

The parameters C_1 and C_2 are different and are functions of temperature, pressure, and membrane porosity and tortuosity. The exponent *m* embodies the effect of pore size, and is the key parameter in modeling different pore sizes in a pore-size distribution. It is referenced throughout the results section. The slopes of the lines in Figure A.3 determine the value of *m*, which equals two for viscous flow, one for Knudsen flow, and zero for molecular diffusion. For Knudsen-molecular diffusion, *m* is between zero and one and for combined Knudsen-viscous flow, *m* is between one and two. Mathematically, one can find *m* by plotting $\ln d_p$ vs. $\ln D_{eff}$ and taking the derivative at each point.

A.3.2 Pore-size distribution model

The transport coefficients above are for a membrane with a single pore size. This is integrated over all pore sizes in the distribution using a model similar to that of Lagana et al. [174] and Martinez et al. [181]. The mass flux through the membrane is the sum of the mass transfer rate through the pores of each pore size interval, *i*, divided by the membrane area. For direct-contact MD, the flux is:

$$n_{1} = \frac{-\frac{M_{1}}{RT} \sum_{i=1}^{N} \left[D_{K-M,i} A_{i} f_{i} \Delta d_{p,i} \right] \nabla p_{1}}{A}$$
(A.12)

where $\Delta d_{p,i}$ is the size of each interval *i*, *N* the total number of size intervals (in this analysis, *N* = 400), and the product of f_i and $\Delta d_{p,i}$ is the fraction of total pores in each size interval. The transport coefficient ($D_{K-M,i}$) is calculated for each size interval using that interval's pore size ($d_{p,i}$) in Eq. (A.7). Assuming cylindrical pores, the membrane surface area for each interval is:

$$A_{\rm i} = \frac{1}{\varepsilon} \frac{\pi d_{\rm p,i}^2}{4} \tag{A.13}$$

and the total membrane area is:

$$A = \frac{1}{\varepsilon} \sum_{i=1}^{N} \frac{\pi d_{p,i}^2}{4} f_i \Delta d_{p,i}$$
(A.14)

The single-pore-size model assumes the same pore area, implying equivalent porosities but a different total number of pores. The mass flux for the single-pore-size model is then:

$$n_{1}^{*} = -\frac{M_{1}}{RT} D_{\mathrm{K-M}}^{*} \nabla p_{1}$$
(A.15)

where D^* represents the transport coefficient based on the mean pore size.

Combining Eqs. (A.12- A.15) and canceling like terms results in:

$$n_1 = \alpha_{\rm PSD} n_1^* \tag{A.16}$$

where α_{PSD} is termed the pore-size-distribution correction factor, defined for direct-contact MD as:

$$\alpha_{\text{PSD,DCMD}} = \frac{\sum_{i=1}^{N} D_{K-M,i} A_i f_i \Delta d_{p,i}}{D_{K-M}^* A}$$
(A.17)

This term is the ratio of the mass flux considering pore-size distribution to the flux based on a mean pore size. Inherent in this definition is that the driving force remains the same between the two models, and thus cancels. This assumption is discussed at the end of this section.

The derivation for vacuum MD is not shown. It is similar to the direct-contact MD derivation above with ∇p replacing ∇p_1 and D_{K-V} replacing D_{K-M} :

$$\alpha_{\text{PSD,VMD}} = \frac{\sum_{i=1}^{N} D_{K-V,i} A_i f_i \Delta d_{\text{p},i}}{D_{K-V}^* A}$$
(A.18)

The air-gap MD equation adds the air-gap resistance to Eq. (A.12):

$$n_{1,\text{AGMD}} = \frac{-\frac{M_{1}}{RT} \left[\frac{\delta_{\text{mem}}}{\sum_{i=1}^{N} D_{\text{K}-\text{M},i} A_{i} f_{i} \Delta d_{\text{p},i}} + \frac{y_{2,\text{LM}} \delta_{\text{gap}}}{D_{12} A} \right]^{-1} \Delta p_{1}}{A}$$
(A.19)

where δ_{mem} and δ_{gap} are the membrane and air-gap thicknesses, which here is assumed to be 100 μ m and 1 mm, respectively. Note that Eq. (A.19) now uses the vapor pressure difference (Δp_1)

and the log-mean mole fraction of air, $y_{2,LM}$, in the gap space resistance and to replace y_2 in Eq. (A.7). Dividing this by an equation for the single-pore-size model gives:

$$\alpha_{\text{PSD,AGMD}} = \frac{\left[\frac{\delta_{\text{mem}}}{\sum_{i=1}^{N} D_{K-M,i} A_i f_i \Delta d_{p,i}} + \frac{y_{2,LM} \delta_{gap}}{D_{12} A}\right]^{-1}}{\left[\frac{\delta_{\text{mem}}}{D_{K-M}^* A} + \frac{y_{2,LM} \delta_{gap}}{D_{12} A}\right]^{-1}}$$
(A.20)

for the pore-size-distribution correction factor for air-gap MD.

If rewritten using Eq. (A.11), the equations for both direct-contact and vacuum MD are the same, which shows the importance of the exponent m:

$$\alpha_{\rm PSD} = \frac{\sum_{i=1}^{N} d_{\rm p,i}^{m_i} d_{\rm p,i}^2 f_i \Delta d_{\rm p,i}}{d_{\rm p,mean}^m \sum_{i=1}^{n} d_{\rm p,i}^2 f_i \Delta d_{\rm p,i}}$$
(A.21)

where this analysis uses μ_g for $d_{p,mean}$. Note that the exponent m_i in the numerator is different for each pore size and is not the same as the exponent m in the denominator corresponding to the mean pore size. This is discussed in Section A.4.1.

One assumption inherent in Eqs. (A.16- A.21) warrants some additional discussion. It is assumed that the driving forces across the membrane are the same for both the single-pore-size and pore-size-distribution models, implying the same temperature profile across the membrane in each case. Due to the latent heat carried with the vapor, increasing mass transfer leads to higher temperature polarization, which then modulates mass transfer. The extent of this modulation is a function of many variables (feed and permeate flow rates, dimensions of module, etc.). The analysis is kept general by neglecting temperature polarization, as including heat transfer

requires knowledge of the entire process under consideration. This analysis is thus the upperbound limiting case, as any increase in temperature polarization will modulate the increase in flux. An MD modeler should thus consider both the results presented here for the limiting case and the specifics for the particular problem at hand. It may therefore be more appropriate to say that the pore-size-distribution correction factor represents the ratio between the membrane mass transfer coefficients as opposed to the overall mass flux and in the case of air-gap MD, the ratio of the membrane-plus-air-gap transport coefficients.

A.3.3 Comparison with other models

The chosen model form is compared with other models from the literature. In particular, many different models are used to combine Knudsen and viscous flow in what is called transition flow. Some have used the formulation used here [194], while others have used a similar formulation with a correction factor added to the Knudsen term (sometimes referred to as the 'slip' term) [125, 195, 196]. Still others use a formulation with transitions between distinct flow regions where certain mechanisms (e.g., Knudsen flow) are absent [114, 177]. Similar formulations exist for combined Knudsen-molecular diffusion [115, 176, 178]. These formulations assume a physical transition exists between the different flow regions, like the transition between laminar and turbulent flow.

The transition-flow formulations are compared in Figure A.4. The model of Imdakm et al. [177], shown with the dashed line, transitions between viscous and Knudsen flow at Kn = 1, where the transport coefficient changes by a factor of five. The models of Creutz [195] and Present [196], both modified by a porosity and tortuosity factor, are shown with the open circles and squares, respectively. Creutz's empirical model is a fit to the experimental data of Knudsen [197, 198], which ranges from Kn = 10^{-4} to Kn = 10^{3} . Present derives his equation with kinetic-

theory arguments and states that it is valid for Kn < 1, with the equation used in this paper without a correction factor being more accurate for Kn > 1. Except for the model based on a transition Knudsen number, the differences between these models are small.



Figure A.4: Effective transport coefficients for vacuum MD for water vapor. Calculated for water vapor transport with $p = p_1 = 3.14$ kPa, $T = 25^{\circ}$ C, $\varepsilon = 0.7$, $\tau = 2$, and $\eta = 9.87 \times 10^{-6}$ kg m⁻¹ s⁻¹.

A similar model used by Khayet et al. [114] uses Knudsen flow for Kn > 10, viscous flow for Kn < 0.01, and the same model as used here in between. At the extreme values of Knudsen number, there is little difference between the transition flow equation used here and the equation for pure Knudsen flow (Kn > 10) or pure viscous flow (Kn < 0.01). Thus, this model is very similar to that used here. However, these transition Knudsen numbers are unnecessary since the full equations take care of 'neglecting' one flow or the other by themselves at either small or large Knudsen number.

Models using transition Knudsen numbers for Knudsen-molecular diffusion [115, 176] are compared in Figure A.5. In these models, transition is assumed to take place between Knudsen and combined Knudsen-molecular diffusion at Kn = 1. This leads to an instantaneous increase in the transport coefficient with *increasing* Knudsen number, which is contrary to each of the transport coefficients in Eqs. (A.5- A.7). The use of this model can cause confusion; the line for the two-region-model formulation in Figure A.5 led some to conclude that smaller pore sizes can result in higher fluxes [199]. When only one equation is used, there is no confusion about what transition Knudsen numbers to use. This is not to suggest that the model used here is ideal. All models are approximations, including the model in this paper. One key point is that all the formulations discussed above have the same dependence on the pore size through the exponent *m*, which is always between zero and two. None of the models take us out of this range for *m*. Thus the generalized results discussed in Section A.4.1 in some sense apply to all the model formulations discussed above, with the shape of the curve between the two endpoints changing slightly depending on the assumed model.



Figure A.5: 'Region' model used in studies on pore-size distribution for direct-contact MD [115, 176]. Calculated for water vapor transport with p = 100 kPa, $T = 25^{\circ}$ C, $p_1 = 3.14$ kPa (saturation at 25°C), $\varepsilon = 0.7$, $\tau = 2$, and $\eta = 9.87 \times 10^{-6}$ kg m⁻¹ s⁻¹.

A.3.4 Analysis method

Three approaches are used to answer the question of whether or not pore-size distribution needs to be considered to accurately model vapor transport in MD: (1) comparing the effect of pore size distribution to the range of reported mass transfer coefficients and uncertainties from MD experiments, (2) comparing the effect of pore-size distribution in MD to its effect on other transport processes using similar membranes, and (3) calculating the error by neglecting poresize distribution in modeling different MD configurations for a range of pore sizes. The method is based on the calculation of α_{PSD} using Eqs. (A.17), (A.18), and (A.20), as summarized in Figure A.6. A comparison of α_{PSD} with unity estimates the importance of pore-size distribution. The further from unity, the more important the pore-size distribution is, or looked at another way, the further from unity, the larger the error when modeling using a single pore size.



Figure A.6: Calculation steps for the pore-size-distribution correction factor.

The first comparison is made with experimental results and uncertainties. For this, one more quantity is calculated: the membrane mass-transfer coefficient. For direct-contact and vacuum MD, this is:

$$K_{\rm mem} = \alpha_{\rm PSD} \, \frac{M_1}{RT} \frac{D_1^*}{\delta_{\rm mem}} \tag{A.22}$$

where, as in Eq. (A.19), D_1^* for direct-contact MD is calculated with the log-mean mole fraction of air ($y_{2,LM}$) in place of y_2 . The range of values from Eq. (A.22) for different geometric standard deviations are compared to the following experimental results: (1) the range in experimentallymeasured mass transfer coefficients for the membranes listed in Table A.1, (2) reported experimental uncertainties, and (3) model uncertainties by propagating the uncertainties in porosity, tortuosity factor, and membrane thickness through to the overall mass transfer coefficients. The purpose here is to see how large the effect of the initially uncertain pore-size distribution is compared to other uncertainties, both uncertainties in modeling and experimental uncertainties. Roughly speaking, is it worth spending effort on improving the measurement and modeling of the pore size distribution? Or is that effort better spent elsewhere?

The second comparison is made with other membrane processes by calculating α_{PSD} for liquid permeation and gas permeation (or flow, such as in aeration processes). The liquid permeation calculation assumes all viscous flow by using Eq. (A.18) with D_V replacing D_{K-V} , which is the same model often used for microfiltration and ultrafiltration in the literature [200, 201]. Gas permeation uses Eq. (A.18) with pressure set to ambient. This is not exact, as the presence of other gases in a mixture may influence the flux, but it is a good approximation. Assuming the same membrane as that for MD implies that liquid permeation refers to microfiltration as opposed to ultrafiltration or reverse osmosis, and gas separation refers to gas transport through porous membranes, as opposed to gas separations via solution-diffusion, or other gas-permselective membranes.

This analysis also determines the effect of pore-size distribution on different MD configurations for different pore-size distribution widths (σ_g) and mean pore sizes, and determines when pore-size distribution can be ignored. Finally, it looks at the effect of pore-size distribution on a membrane heat pump by incorporating the above equations into the model from Chapter 4. This latter example will also quantify the impact of temperature and concentration polarization relative to the impact of pore-size distribution, but only for the specific module configuration and process case presented.

A.4 Results and discussion

A.4.1 Generalized results

This section looks at how the effect of pore-size distribution on mass transfer depends on the exponent *m*. This partially answers why neglecting pore-size distribution affects each membrane process and each MD configuration differently. Figure A.7 shows m as a function of the Knudsen number for both combined Knudsen-molecular diffusion and combined Knudsenviscous flow. A single line is shown for Knudsen-viscous flow, which is weakly dependent on temperature when plotted against Knudsen number, whereas two lines are shown for Knudsenmolecular flow, where the temperature has a larger effect. There are two key points here. First, the dependence on pore size is always larger for Knudsen-viscous flow than for Knudsenmolecular diffusion; that is, $m \ge 1$ for the former while $m \le 1$ for the latter. This implies that pore-size distribution is more important for vacuum MD than for direct contact MD. Second, increasing the mean pore size plays an important role in both transport mechanisms. Since the Knudsen number is inversely proportional to the pore size, as the pore size decreases, this m exponent approaches the Knudsen limit of m = 1. For larger pore sizes (small Kn), vacuum MD approaches the viscous limit of m = 2 and direct contact MD approaches the molecular diffusion limit of m = 0. As discussed in Sections A.4.3 and A.4.4, though, the Knudsen number is always above 1 for all practical pore sizes in vacuum MD, and the flow stays near the Knudsen limit of m = 1.



Figure A.7: Exponent *m* in Eq. (A.11) vs. Knudsen number for diffusion (direct-contact MD) at 100 kPa and two different temperatures (25 and 70°C) and for pressure-driven flow (vacuum MD) at 3.14 kPa and 25° C.

Figure A.8 plots the pore-size-distribution correction factor vs. m using Eq. (A.21) for normal and log-normal distributions for two different geometric standard deviations. This plot is still independent of the type of flow since the exponent m carries this information. Two lines are shown for each distribution. The dashed line is an approximation assuming m_i equals the mean pore size value (m in the denominator of Eq. (A.21)) for all values of i. The solid line uses Eq. (A.21) with the appropriate m_i for each pore size. (Note that Sections A.4.2 through A.4.5 use the full equations (Eq. A.17, A.18, A.20) with no approximations.) There is a difference between the approximation and the actual value since the flux is dominated by transport through larger pores. For m < 1, the average *m* is greater than the value of m_i for the larger pores (cf. Figure A.7), and therefore the approximation is greater. For m > 1, the average *m* is less than the value of m_i for larger pores, and therefore the approximation is less. Also, the larger magnitude of *m* makes the difference more significant.

For direct-contact and air-gap MD, the analysis assumes ambient pressure and a certain isothermal temperature. For a pore size of 100 nm (near Kn = 1), the value of *m* in Figure A.7 at the higher temperature is 20% higher than at the lower temperature, which translates into a 4% higher α_{PSD} (Figure A.8) for $\sigma_g = 1.5$. The general trend of changing operating conditions is that increasing temperature or decreasing pressure pushes the Knudsen-molecular line in Figure A.7 towards the Knudsen line of *m* = 1. At the extreme, with no air present in the pores, *m* is slightly less than 1 for a pore size of 100 nm. This implies that operating direct-contact MD with the air evacuated from the pores will be more in line with the vacuum MD results presented below as opposed to the direct-contact MD results, which are for atmospheric pressure operation.



Figure A.8: Pore-size-distribution correction factor as a function of the exponent *m*. The lines for $\sigma_g = 1.2$ have a similar shape to $\sigma_g = 1.5$. The x-axis label refers to *m* for the mean pore size. Dashed lines represent approximate solution with m_i a constant.

The trends exhibited by the approximate solutions in Figure A.8 illustrates that the exponent *m* in a transport process's governing equation is a good indicator of the effect of pore size distribution in modeling. Note also that including the effects of pore-size distribution always predicts higher transport coefficients when using the complete transport model, as opposed to the 'region' models discussed in Section A.3.3, regardless of the shape of the distribution. The effect is larger for the log-normal distribution than for a symmetric distribution since the log-normal distribution is skewed towards larger pore sizes, but the effect for a symmetric distribution can still be important because the larger pore sizes are weighted by the larger pore areas (A_i) in Eq. (A.12). All results presented in Sections A.4.2 through A.4.5 use the log-normal distribution.

A.4.2 Comparison with experimental results

The purpose of this section is not to validate the model. The dusty-gas model has been shown to accurately predict MD flux many times in the literature. Rather, the focus is on comparing the ranges in experimental values and experimental uncertainties to the difference between modeling a single pore size and modeling a pore-size distribution.

The first four membrane 'columns' in Figure A.9 show the spread of experimental masstransfer coefficients for direct-contact MD from several studies in the MD literature. The authors of these studies have already removed the effects of concentration and temperature polarization with an assumed correlation for the internal boundary-layer coefficients. The GVHP and HVHP membranes are thicker and thus have smaller mass transfer coefficients, in general, than the TF-200 and TF-450 membranes.

The theoretical effect of pore-size distribution is shown by the solid, I-beam lines directly to the right of the data, where σ_g for a log-normal distribution is varied from 1 to 2 to calculate K_{mem} in Eq. (A.22). These values likely overestimate the pore-size distribution effect, as geometric standard deviations for commercially-available membranes are often less than 1.2. The dotted I-beam lines show the uncertainties in the experimentally-measured membrane mass transfer coefficients reported by Martinez et al. [131]. These uncertainties are on the same order of magnitude as the maximum effect of pore-size distribution for direct-contact MD. The dashed I-beam line shows the uncertainty in the modeled membrane mass transfer coefficient using uncertainties in the membrane porosity, thickness, and tortuosity factor. It appears that for these membranes with mean pore sizes ranging from 0.2 to 0.45 µm, the predicted effect of pore-size distribution is small relative to variation in the experimentally-measured transport coefficients,

experimental uncertainties, and model uncertainties. Thus, any effect of pore size distribution in direct-contact MD will be difficult to distinguish versus other experimental and modeling uncertainties.



Figure A.9: Comparison of effects of pore-size distribution to experimental results. Experimental data points [112, 115, 131, 179, 181, 186, 202-204] shown with open circles. Range of K_{mem} values from Eq. A.20 for $\sigma_g = 1$ (single pore model) to $\sigma_g = 2$ (log-normal distribution); experimental uncertainties; and modeling uncertainties are shown, respectively, in the solid, dotted, and dashed I-beam lines next to the experimental data. The first four membrane 'columns' are for direct-contact MD; final membrane 'column' is for vacuum MD.

For vacuum MD (the final membrane 'column' in Figure A.9), a literature search found no reported uncertainties and one experimental data point for a test performed by Khayet et al. [186]. In this case, the value of m is near one and the effect of pore-size distribution is much larger than for direct contact MD where m is between 0.2 and 0.4. The uncertainty due to membrane porosity, tortuosity factor, and thickness is shown in the dashed I-beam, which is much smaller than the theoretical effect of pore-size distribution. Thus, for vacuum MD, the predicted effect of pore-size distribution can be larger than the uncertainty in modeling.

A.4.3 Comparison to other membrane processes

Similar to the comparison with experimental results above, a comparison with other transport processes is another way to gauge the importance of pore-size distribution in MD. These comparisons are meant to be more qualitative than quantitative. The effects of pore-size distribution on microfiltration and gas permeation are not the focus of this paper and are influenced by other factors, such as concentration polarization. These are, nonetheless, appropriate benchmarks for comparison. Figure A.10 shows the pore-size distribution correction factor assuming a geometric mean pore diameter of 0.2 μ m. Moving to larger or smaller mean pore diameters will shift the lines, but the overall trend remains the same. For a geometric standard deviation of 1.2, the transport coefficient for liquid permeation (m = 2) is 22% larger than a single-pore-size model, whereas for direct-contact MD ($m \approx 0.3$) the difference is less than 3%, which shows m to be a useful predictor of the effect of pore size distribution. It also shows that liquid permeation has the highest sensitivity to pore-size distribution, implying it should be the most responsive technique for identifying differences in the distribution of pore sizes for membranes with equivalent mean pore size and porosity.

Although both vacuum MD and gas permeation are pressure driven gas flows, vacuum MD operates at low pressures (Kn ~ 20) while gas permeation operates near ambient pressure (Kn ~ 0.6). The Knudsen + viscous line in Figure A.7 shows that for pressure-driven processes, *m* is about 15% higher for gas permeation (Kn ~ 0.6) since a higher percentage of the total flux is due to viscous flow at the higher pressure. In Figure A.8, the values of *m* from Figure A.7

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correlate to a 20% higher α_{PSD} . Note, though, that reducing the pore size increases Knudsen flow in gas permeation and pushes its line in Figure A.10 towards the line for vacuum MD, which is nearly all Knudsen flow for all pores sizes.



Figure A.10: Effect of pore-size distribution (σ_g) on different membrane processes. p = 100 kPa, $T = 25^{\circ}$ C, $p_1 = 3.14$ kPa (saturation at 25°C), $\mu_g = 0.2 \ \mu m \ \varepsilon = 0.7$, $\tau = 2$, and $\eta = 9.87 \times 10^{-6} \ \text{kg m}^{-1}$ s⁻¹ (for vapor). For liquid permeation, α_{PSD} does not depend on η since it is the same for all pore sizes and viscous flow is the only mechanism present.

A.4.4 Effect on different MD configurations

Figure A.11 shows the pore-size distribution correction factor for direct-contact, air-gap, and vacuum MD for different values of the mean pore size. Both $\sigma_g = 1.5$ (solid lines) and $\sigma_g = 1.2$ (dashed lines) are shown. The shapes of the lines are consistent for other standard deviations.

In selecting the minimum pore size for this figure, there were conflicting interests to (1) represent all possible pore sizes for MD while (2) avoiding very small pore sizes where other transport mechanisms (e.g., surface diffusion) become important. Here 0.05 microns is used. This captures nearly all pore sizes listed in MD review articles for membranes used in MD research experiments [15, 18, 19] and avoids the region (<0.02 microns) where Fujii et al. [205, 206] suggested surface diffusion is significant.

For vacuum MD, Knudsen flow dominates for all potential pore sizes and thus α_{PSD} is nearly constant. The error by neglecting pore-size distribution in vacuum MD is 9% for $\sigma_g = 1.2$ and over 50% for $\sigma_g = 1.5$. For direct-contact MD, *m* and therefore α_{PSD} increase with decreasing pore size as Knudsen diffusion becomes more and more important. For a mean pore size of 50 nm, the error can be as high as 28% for $\sigma_g = 1.5$. Commercial membranes commonly used in direct-contact MD have a pore size on the order of 100 nm and a relatively narrow pore size distribution ($\sigma_g = 1.2$), which results in an error of 3.5%. For air-gap MD, assuming a gap width of 1 mm, the error is less than 7% for all considered cases, and less than 1% for a membrane with $\sigma_g = 1.2$ and pore sizes near 100 nm. These results depend on the air gap width, with a doubling of the air-gap width roughly halving the percent error.

Figure A.11 illustrates the difference between modeling MD with a membrane with both a relatively narrow ($\sigma_g = 1.2$) and wide pore-size distribution ($\sigma_g = 1.5$). Note that there is a possibility of even wider distributions ($\sigma_g \approx 2$), especially for lab-made membranes. Thus, the large difference between the errors shown for the two standard deviations in Figure A.11, and the difference between the far-left and far-right sides of Figure A.10, emphasize that it is still necessary to have at least a rough estimate of the width of the distribution before deciding if that distribution should be included in an MD model. It is best, then, to summarize the results by reporting the errors in vapor flux due to neglecting pore-size distribution *for distributions narrower than a specified value*. This error is less than 5% in the following cases. Vacuum MD: $\sigma_g < 1.07$ for all pore sizes. Direct-contact MD: $\sigma_g < 1.2$ for $d_{p,mean} > 50$ nm. Air-gap MD: $\sigma_g < 1.45$ for $d_{p,mean} > 50$ nm. Keep in mind, though, that these results are conservative, as discussed at the end of Section A.3.2.



Figure A.11: Pore-size distribution correction factor for different MD configurations as a function of geometric mean pore size. $\sigma_g = 1.5$ (solid lines), $\sigma_g = 1.2$ (dashed lines). VMD = vacuum MD, AGMD = air-gap MD, DCMD = direct-contact MD.
A.4.5 *Effects of pore-size distribution on a membrane heat pump*

Inserting the pore-size distribution model outlined above into the heat pump model from Chapter 4 provides a look at the effect of pore-size distribution on heat pump performance. Figure A.12 shows the variation in three heat-pump figures of merit versus the membrane poresize-distribution correction factor. These three parameters are: the overall mass transfer coefficient considering the two membranes and the air gap (not including polarization), the water-vapor flux, and the temperature lift. The x-axis variable ($\alpha_{PSD,DCMD}$) represents the effect of neglecting pore size distribution on just the membrane. It is a function of both the mean pore size and σ_g , as illustrated in Figure A.11.

As a representative example, consider a mean pore size of 200 nm and $\sigma_g = 1.5$, in which case $\alpha_{PSD,DCMD} = 1.12$. The error in neglecting pore-size distribution for the overall mass transfer coefficient is only 5% ($\alpha_{PSD,heat pump} = 1.05$), because the two membranes account for only 45% of this composite mass transfer resistance, with the air gap (assuming an air-gap width of 1 mm) accounting for 55% [207]. This overall resistance does not include temperature and concentration polarization or the effect of varying temperatures and concentrations along the flow channel. These effects are included in the flux calculation, where they limit the increase in flux to only 2.5% for this representative example. Keep in mind that the heat pump requires highly-concentrated salt solutions, and thus the concentration polarization in the heat pump is higher than in most MD cases. An important parameter for the heat pump is the temperature lift (ΔT_{lift}). The indirect effects of pore-size distribution increase this parameter by just over 1%. This analysis shows that pore-size distribution plays a minimal role in modeling a membrane heat pump.

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Figure A.12: Theoretical effect of pore-size distribution on performance of membrane heat pump assuming $\delta_{mem} = 100 \ \mu m$ and $\delta_{gap} = 1 \ mm$. Other values as assumed in [207]. $\alpha_{PSD,heat \ pump} = ratio$ of (membrane + gap + membrane) transport coefficients for pore-size distribution and single-pore-size models; $j_{vapor} =$ water vapor flux; $\Delta T_{lift} =$ heat-pump temperature lift.

A.5 Conclusions

Does pore-size distribution need to be considered when modeling MD? In answering this question, an MD modeler should consider the following conclusions from this analysis:

- (Section A.4.1) The dependence of the governing equation on pore size (the exponent *m* in Eq. A.22) is a good indicator of the effect of neglecting pore-size distribution.
- (Section A.4.2) The uncertainties in modeling and experimental design likely overwhelm any effect from pore-size distribution for direct-contact MD, but not for vacuum MD.

- (Section A.4.3) The effect of neglecting pore size distribution in modeling pressure-driven processes is, in general, much larger than that for diffusion-driven processes.
- (Section A.4.4) The error in vapor flux by neglecting pore-size distribution is strongly dependent on the width of the distribution. It is at most 5% for membranes with distributions narrower than the following. Vacuum MD: $\sigma_g < 1.07$ for all pore sizes. Direct-contact MD: $\sigma_g < 1.2$ for $d_{p,mean} > 50$ nm. Air-gap MD: $\sigma_g < 1.45$ for $d_{p,mean} > 50$ nm. Larger mean pore sizes reduce the error for direct-contact and air-gap MD.
- (Section A.4.5) Neglecting pore size distribution in modeling a membrane heat pump leads to a minimal error in most cases.

Nomenclature for Appendix A

Α	membrane surface area (m^2)
C_1, C_2	constants in Eq. (A.11)
$d_{\mathrm{p,i}}$	membrane pore diameter in interval i (m)
$d_{\rm p,mean}$	geometric mean pore diameter; same as μ_g (m)
D_{12}	molecular diffusion coefficient (m ² s ⁻¹)
$D_{ m eff}$	generic effective transport coefficient for water vapor $(m^2 s^{-1})$
D^*	transport coefficient through membrane pores based on mean pore size $(m^2 s^{-1})$
D_{M}	effective transport coefficient for molecular (ordinary) diffusion $(m^2 s^{-1})$
D_{K}	effective transport coefficient for Knudsen flow $(m^2 s^{-1})$
$D_{ ext{K-M}}$	effective transport coefficient for combined Knudsen-molecular diffusion (m 2 s $^{-1}$)
$D_{ ext{K-V}}$	effective transport coefficient for combined Knudsen-viscous flow ($m^2 s^{-1}$)
$D_{ m V}$	effective transport coefficient for viscous flow, $\kappa p/\eta$ (m ² s ⁻¹)
f_i	probability density function (m ⁻¹)

\dot{J} vapor	diffusive mass flux of vapor (kg m ⁻² s ⁻¹)
Κ	mass transfer coefficient or permeance (kg m ⁻² h ⁻¹ kPa ⁻¹)
Kn	Knudsen number
М	molecular mass (kg kmol ⁻¹)
т	exponent in Eq. (A.11)
n _i	mass flux of component i (kg m ⁻² s ⁻¹)
Ν	number of pore size ranges in distribution functions
р	pressure (kPa)
p_i	partial pressure of component i (kPa)
R	universal gas constant (8314 J mol ⁻¹ K ⁻¹)
Т	temperature (K or ^o C)
<i>Yi</i>	mole fraction of component <i>i</i>
Greek letters	

$\alpha_{\rm PSD}$	ratio of quantity (e.g., flux) considering pore-size distribution to that without
$\delta_{ m mem}$	membrane thickness (m)
$\delta_{ m gap}$	air-gap width (m)
ε	membrane porosity
$\Delta d_{\mathrm{p,i}}$	size of interval <i>i</i> in probability density function (m)
$\Delta T_{ m lift}$	difference between outlet and inlet temperatures of membrane heat pump (K)
η	dynamic viscosity (kg m ⁻¹ s ⁻¹)
К	Darcy's Law permeability (m ²)
λ	molecular mean free path (m)
μ	mean or average

- σ standard deviation
- au membrane tortuosity

subscripts

1, 2	components
a	arithmetic
avg	average value in the pore
eff	effective
g	geometric
i	pore-size interval in probability density function
*	value based on mean pore size

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Appendix B Computational fluid dynamics analysis of natural convection in the air gap

This appendix presents the results of a computation fluid dynamics (CFD) analysis of the mass, momentum, species, and energy equations in the air gap between two rows of hollow fiber membranes. The analysis considers the hollow fiber module in both horizontal and vertical orientations to assess the importance of natural convection on heat and mass transfer between the rows. As discussed in Chapters 4 and 6, the effect of natural convection is negligible for the geometry considered in the experimental prototype modules. The purpose of this analysis is to determine when natural convection is no longer negligible.

B.1 Model

Figure B.1 shows the mesh for this natural convection analysis. Two meshes are used depending on the orientation of the module. The horizontally-oriented mesh includes several hollow fibers to ensure that the domain captures any natural convection cells. It also includes two rows of both the hot and cold hollow fibers to include the buoyancy effects around the bottom of the hot tubes and the top of the cold tubes.

The vertically-oriented mesh includes a long air gap section between two rows of fibers, with symmetry assumed at the centerline of the hollow fiber rows and a periodic condition assumed at the sides. The top and bottom include a large adiabatic region to separate the region of interest from the inlets and outlets. A pressure is specified at the top and bottom boundary, with Fluent solving for the velocities at the boundaries.



(b)

Figure B.1: Mesh used for CFD analysis of air gap natural convection. (a) horizontal orientation, (b) vertical orientation.

The model uses the mass, momentum, energy, and species equations. The species in this case is water vapor. The boundary conditions at the hollow-fiber walls are constant temperature and constant water vapor concentration. The water vapor concentration is assumed to be saturated at the cooler water side, and at 30% relative humidity on the hotter absorbent solution side.

Two runs in the vertical orientation with a 5 mm air gap found the effects of water vapor transport at the membrane surface to be negligible. The two runs were: (1) with the species equation, and (2) without the species equation. The difference in the heat transfer between the fiber rows in these two cases was 0.4%.

Three geometries were analyzed: a base case, a small fiber case, and a wide spacing case (Table B.1). Each of these geometries is simulated for the vertical and horizontal orientations. The base case geometry is very near the hollow fiber v.1 prototype. The outer fiber diameter is 0.5 mm, the air gap width 1 mm, and the fiber spacing 0.75 mm. After each simulation, the model is 'scaled' in each dimension and then a new simulation is run. The non-dimensional geometry remains the same: $z/d_o = 3$, $t/d_o = 1.5$, but the absolute values of the fiber diameter, the gap width, and the fiber spacing increase for each run. For example, the first run is for the fiber outer diameter, air gap width, and fiber spacing specified above, the second simulation is scaled by three so that these values change to 1.5 mm, 3 mm, and 2.25 mm, and the third simulation scaled by four, and so on. Similar sets of 'scaled' simulations are performed for the small-fiber and wide-spacing cases.

First-run dimensions	Base case	Small fibers	Wide spacing
Fiber outer diameter, d _o (mm)	0.5	0.2	0.5
Air-gap width, d _{gap} (mm)	1	1	1
Fiber spacing, t (mm)	0.3	0.75	1.25
Row spacing, z (mm)	1.5	1.2	1.5
Non-dimensional geometry			
t / d _o	1.5	1.5	2.5
z / d _o	3	6	3

Table B.1: Geometries for CFD natural convection simulations. Note that $z = d_{gap} + d_o$

B.2 Results

The following three figures show the temperature profiles and velocity vectors for the base-case geometry. At an air-gap width of 1 mm, natural convection in both cases is negligible, confirming that natural convection should be negligible in the prototype module, where $d_{gap} = 0.91$ mm.

The temperature profile between the two rows of fibers for the 1-mm air gap case is shown in Figure B.2. This temperature profile is the same as when the buoyancy terms are ignored, and the calculated heat fluxes for the two cases are within 0.5%.

Similar results were obtained for the vertical orientation for an air gap width of 1 mm. But natural convection increases the heat flux compared to the conduction-only case as the air gap increases. Figure B.3 shows the temperature profile and velocity vectors for the vertical orientation for a 5-mm air gap case. A long natural convection cell develops, with less dense air rising next to the warmer fibers on the right, and denser air falling next to the cooler fibers on the left.

For the horizontal orientation, natural convection does not develop until air gap widths are near 10 mm. Figure B.4 shows the temperature profile and velocity vectors for the horizontal orientation for this 10-mm air gap case. Natural convection cells develop around the heated fibers, with warmer rising air interspersed with cooler, falling air from the cooler fibers above.



Figure B.2: Temperature profile for base-case geometry scaled by one (1-mm air gap): (a) no buoyancy term, and (b) with buoyancy term. The two temperature profiles are the same, indicating natural convection is negligible.





Figure B.3: (a) Temperature profile and (b) velocity vectors for vertical orientation for base-case geometry scaled by five (5-mm air gap).



Figure B.4: (a) Temperature profile and (b) velocity vectors for horizontal orientation for basecase geometry scaled by ten (10-mm air gap).

Figure B.5 summarizes the results by plotting the increase in heat transfer due to natural convection for the horizontal and vertical orientations for the base-case geometry. Natural convection is always present in the vertical orientation; there is no critical Rayleigh number for when natural convection begins. However, for the air-gap width of the prototype (0.91 mm), the increase in heat transfer due to this natural convection is negligible. Natural convection could be considered 'non-negligible' at around an air gap width of 5 mm, where the heat transfer increases by nearly10%.

For the horizontal case, natural convection is absent until air gap widths of around 10 mm. For the 20 K temperature difference used here, this gives a Rayleigh number based on the air-gap width of around 2200. For the 9 mm air-gap run, where there was no natural convection, the Rayleigh number was just over 1600. These results are consistent with the simple parallel plate geometry, heated from the bottom, where the critical Rayleigh number is 1708 [143]. This implies that the complex air gap geometry has a small influence on natural convection, and the air gap width is an appropriate dimension for gauging the important of natural convection.

When plotted against the air gap width, results obtained on simulations of small fiber and wide spacing geometries were very similar to those for the base case geometry. This again shows the air gap width to be the appropriate dimension, at least for the geometries considered here $(t/d_o < 2.5, z/d_o < 6)$.



Figure B.5: Increase in heat transfer due to natural convection in the air gap over the conductiononly case for horizontal and vertical orientations. Natural convection in both cases negligible for prototype geometry ($d_{gap} = 0.9$ mm). Heat transfer in vertical orientation increases continuously with gap width due to natural convection, while heat transfer in horizontal orientation stays near conduction-only value until reaching the critical Rayleigh number near a gap width of 10 mm. $z/d_o = 3$ and $t/d_o = 1.5$.

Appendix C

Scaling analysis for internal boundary-layer flow

This appendix expands on the scaling analysis from Chapter 4, adding an explanation of the scale factors used to non-dimensionlize the governing equations and a derivation of the nondimensionalized equations. It starts by repeating the governing equations for the internal, boundary layer flow, with a more detailed derivation of the equations and the scale factors to follow.

C.1 Governing equations

This section repeats the first sets of equations from Chapter 4. The governing equations for internal flow are:

mass:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{C.1}$$

x-momentum:

$$u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = -\frac{1}{\rho}\frac{\partial P}{\partial x} + v\left[\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right] - g_x\beta\left(T - T_{ref}\right) - g_x\beta_M\left(\omega_1 - \omega_{1,ref}\right)$$
(C.2)

y-momentum:

$$u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y} = -\frac{1}{\rho}\frac{\partial P}{\partial y} + v\left[\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2}\right] - g_y \beta \left(T - T_{ref}\right) - g_y \beta_M \left(\omega_1 - \omega_{1, ref}\right)$$
(C.3)

energy:

$$u\frac{\partial T}{\partial x} + v\frac{\partial T}{\partial y} = \alpha \left[\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2}\right] + \frac{1}{\rho c_p} \dot{q}''' + \frac{\mu}{\rho c_p} \left(\frac{\partial u}{\partial y}\right)^2$$
(C.4)

species 1:

$$u\frac{\partial\omega_1}{\partial x} + v\frac{\partial\omega_1}{\partial y} = D_{12}\left[\frac{\partial^2\omega_1}{\partial x^2} + \frac{\partial^2\omega_1}{\partial y^2}\right]$$
(C.5)

In these equations, P is the non-hydrostatic pressure, υ the kinematic viscosity, β the thermal expansion coefficient, β_M the concentration expansion coefficient, α the thermal diffusivity, and D_{12} the mass diffusivity for salt in water, and \dot{q}''' the internal heat generation due to the heat of mixing.

The boundary conditions for the above equations are:

at
$$x = 0$$
: $u = U_0; v = 0; T = T_{in}; \omega_s = \omega_{s,in}$ (C.6)

at y = -H:

$$u = 0; v = V_{wall}(x) = \frac{K}{\rho_w} (p_{v,\infty} - p_v) \qquad (C.7)$$

$$-k \frac{dT}{dy} = KH_{vapor} (p_{v,\infty} - p_v) + U(T_{\infty} - T)$$

$$-\rho D_{12} \frac{d\omega_s}{dy} = K (p_{v,\infty} - p_v)$$
at x = L:

$$u = f_1(y); v = f_2(y); T = f_3(y); \omega_s = f_4(y) \qquad (C.8)$$

$$P(L, y) = P_{out}$$
at y = H:

$$u = 0; v = -V_{wall}(x) = -\frac{K}{\rho_w} (p_{v,\infty} - p_v)$$

$$k \frac{dT}{dy} = KH_{vapor} (p_{v,\infty} - p_v) + U(T_{\infty} - T)$$

$$\rho D_{12} \frac{d\omega_s}{dy} = K (p_{v,\infty} - p_v)$$

where U_0 , T_0 , and $\omega_{s,0}$ are the inlet velocity, temperature, and mass fraction, $V_{wall}(x)$ is the flux through the wall due to vapor transfer, K is the mass transfer coefficient, H_v is the water enthalpy

at T_{∞} , $f_1(y)$, $f_2(y)$, $f_3(y)$, and $f_4(y)$ are unknown functions, and P_{out} is the outlet pressure. The following dimensionless variables are introduced with unspecified scale factors:

$$x^* = \frac{x}{x_s}; \ y^* = \frac{y}{y_s}; \ u^* = \frac{u}{U_0}; \ v^* = \frac{v}{V_{wall,0}}$$
 (C.10)

$$T^* = \frac{T - T_0}{T_s}; \ \omega_1^* = \frac{\omega_1 - \omega_{1,0}}{\omega_{1,s}}; \ p_v^* = \frac{p_v - p_{v,\infty}}{p_{v,0} - p_{v,\infty}}$$
(C.11)

$$\left(\frac{\partial u}{\partial x}\right)^* = \frac{x_s}{\Delta U_x} \frac{\partial u}{\partial x}; \left(\frac{\partial u}{\partial y}\right)^* = \frac{y_s}{\Delta U_x} \frac{\partial u}{\partial y}$$
(C.12)

$$\left(\frac{\partial v}{\partial x}\right)^* = \frac{x_s}{\Delta V_x} \frac{\partial v}{\partial x}; \left(\frac{\partial v}{\partial y}\right)^* = \frac{x_s}{\Delta V_y} \frac{\partial v}{\partial y}$$
(C.13)

$$\left(\frac{\partial P}{\partial x}\right)^* = \frac{x_s}{\Delta P_x} \frac{\partial P}{\partial x}; \left(\frac{\partial P}{\partial y}\right)^* = \frac{y_s}{\Delta P_y} \frac{\partial P}{\partial y}$$
(C.14)

$$\left(\frac{\partial T}{\partial x}\right)^* = \frac{x_s}{\Delta T_x} \frac{\partial T}{\partial x}; \left(\frac{\partial T}{\partial y}\right)^* = \frac{y_{th}}{\Delta T_y} \frac{\partial T}{\partial y}$$
(C.15)

$$\left(\frac{\partial \omega_{l}}{\partial x}\right)^{*} = \frac{x_{s}}{\Delta \omega_{l,x}} \frac{\partial \omega}{\partial x}; \left(\frac{\partial \omega_{l}}{\partial y}\right)^{*} = \frac{y_{M}}{\Delta \omega_{l,y}} \frac{\partial \omega}{\partial y}.$$
(C.16)

C.2 Non-dimensionalizing the governing equations

This section takes the governing equations and boundary conditions, as presented above and in Chapter 4, and shows how the scale factors lead to the dimensionless equations at the end of Section 4.2.9.

Substituting the scaled factors into the governing equations leads to the dimensionless form of the equations:

mass:

$$\frac{\Delta U_x}{x_s} \left(\frac{\partial u}{\partial x}\right)^* + \frac{\Delta V_y}{y_s} \left(\frac{\partial v}{\partial y}\right)^* = 0$$
(C.17)

x-momentum:

$$\frac{U_{0}\Delta U_{x}}{x_{s}}u^{*}\left(\frac{\partial u}{\partial x}\right)^{*} + \frac{V_{wall,0}\Delta U_{y}}{y_{s}}v^{*}\left(\frac{\partial v}{\partial y}\right)^{*} = -\frac{\Delta P_{x}}{x_{s}\rho}\left(\frac{\partial P}{\partial x}\right)^{*} + \upsilon\frac{\Delta U_{x}}{x_{s}^{2}}\frac{\partial}{\partial x^{*}}\left(\frac{\partial u}{\partial x}\right)^{*} + \upsilon\frac{\Delta U_{y}}{y_{s}^{2}}\frac{\partial}{\partial y^{*}}\left(\frac{\partial u}{\partial y}\right)^{*} - g_{x}\beta\Delta T_{y}T^{*} - g_{x}\beta_{M}\Delta\omega_{1,y}\omega_{1}^{*}$$
(C.18)

y-momentum:

$$\frac{U_{0}\Delta V_{x}}{x_{s}}u^{*}\left(\frac{\partial v}{\partial x}\right)^{*} + \frac{V_{wall,0}\Delta V_{y}}{y_{s}}v^{*}\left(\frac{\partial v}{\partial y}\right)^{*} = -\frac{\Delta P_{y}}{y_{s}\rho}\left(\frac{\partial P}{\partial y}\right)^{*} + v\frac{\Delta V_{x}}{x_{s}^{2}}\frac{\partial}{\partial x^{*}}\left(\frac{\partial v}{\partial x}\right)^{*} + v\frac{\Delta V_{y}}{y_{s}^{2}}\frac{\partial}{\partial y^{*}}\left(\frac{\partial v}{\partial y}\right)^{*} - g_{y}\beta \ \Delta T_{y}T^{*} - g_{y}\beta_{M}\Delta\omega_{1,y}\omega_{1}^{*}$$
(C.19)

energy:

$$U\frac{\Delta T_{x}}{x_{s}}u^{*}\left(\frac{\partial T}{\partial x}\right)^{*} + V\frac{\Delta T_{y}}{y_{T}}v^{*}\left(\frac{\partial v}{\partial y}\right)^{*}$$

$$= \alpha\frac{\Delta T_{x}}{x_{s}^{2}}\frac{\partial}{\partial x^{*}}\left(\frac{\partial T}{\partial x}\right)^{*} + \alpha\frac{\Delta T_{y}}{y_{T}^{2}}\frac{\partial}{\partial x^{*}}\left(\frac{\partial T}{\partial y}\right)^{*} + \frac{1}{\rho c_{p}}\dot{q}''' + \frac{\mu}{\rho c_{p}}\frac{\left(\Delta U_{y}\right)^{2}}{y_{T}^{2}}\left(\frac{\partial u}{\partial y}\right)^{*2}$$
(C.20)

species 1:

$$U_{0} \frac{\Delta \omega_{1,x}}{x_{s}} u^{*} \left(\frac{\partial \omega_{1}}{\partial x}\right)^{*} + V_{wall,0} \frac{\Delta \omega_{1,y}}{y_{M}} v^{*} \frac{\partial}{\partial y^{*}} \left(\frac{\partial \omega_{1}}{\partial y}\right)^{*} =$$

$$D_{12} \frac{\Delta \omega_{1,x}}{x_{s}^{2}} \frac{\partial}{\partial x^{*}} \left(\frac{\partial \omega_{1}}{\partial x}\right)^{*} + D_{12} \frac{\Delta \omega_{1,y}}{y_{M}^{2}} \frac{\partial}{\partial y^{*}} \left(\frac{\partial \omega_{1}}{\partial y}\right)^{*}$$
(C.21)

Note that in the momentum equations, T_{ref} is set equal to the inlet temperature (T₀). Also, the buoyancy terms scale with the y-direction temperature and mass fraction differences since these

differences are what drives the natural convection. The ΔT_y term will be defined from scaling the energy equation, while $\Delta \omega_y$ will be defined from scaling the species equation.

The dimensionless boundary conditions become:

$$x^{*} = 0; \qquad u^{*} = 1; \ v^{*} = 0; \ T^{*} = 0; \ \omega_{s}^{*} = 0 \qquad (C.22)$$

$$y^{*} = -1; \qquad u^{*} = 0 \qquad (C.23)$$

$$v^{*} = \frac{V_{wall}(x)}{V_{wall,0}} = \frac{K(p_{v,\infty} - p_{v}^{*}p_{v,s} - p_{v,\infty})}{\rho_{w}} p_{v}^{*} = \frac{K\Delta p_{v,0}}{\rho_{w}} p_{v}^{*}$$

$$-\left(\frac{dT}{dy}\right)^{*} = \frac{(KH_{vapor}\Delta p_{v,0}p_{v}^{*} + U(T_{s}T^{*} + T_{0} - T_{0}))y_{T}}{k\Delta T_{y}}$$

$$= \frac{(KH_{vapor}\Delta p_{v,0}p_{v}^{*} + UT_{s}T^{*})y_{T}}{k\Delta T_{y}}$$

$$-\left(\frac{d\omega_{1}}{dy}\right) = \frac{K\Delta p_{v,x=0}y_{M}}{\rho_{f}D_{12}\Delta\omega_{s,y}}p_{v}^{*}$$

$$x^{*} = 1: \qquad u^{*} = f_{1}^{*}(y^{*}); \ v^{*} = f_{2}^{*}(y^{*}); \ T^{*} = f_{3}^{*}(y^{*}); \ \omega_{1}^{*} = f_{4}^{*}(y^{*})$$
(C.24)

$$y^{*} = 1: \qquad u^{*} = 0 \qquad (C.25)$$

$$v^{*} = \frac{K\Delta p_{v,0}}{\rho_{w}} p_{v}^{*}$$

$$\left(\frac{dT}{dy}\right)^{*} = \frac{\left(KH_{vapor}\Delta p_{v,x=0}p_{v}^{*} - U\Delta T_{\infty}T^{*}\right)y_{T}}{k\Delta T_{y}}$$

$$\left(\frac{d\omega_{1}}{dy}\right)^{*} = \frac{K\Delta p_{v,x=0}y_{M}}{\rho D_{12}\Delta \omega_{s,y}} p_{v}^{*}$$

where $\Delta p_{v,0} = p_{v,\infty}$ - $p_{v,0}$. Note that y_s is set equal to H and x_s equal to L.

 $P^* = 0$

These equations are cumbersome, but they will be simplified significantly in the next steps. But first, simple arguments are used to obtain three of the four velocity scale factors. The x-velocity changes from 0 at the wall to the maximum velocity at the centerline, and thus the scale $\Delta U_x \sim U_0$ is used. Since $v = V_{wall,0}$ at the wall and v = 0 at the centerline, $\Delta V_y \sim V_{wall,0}$. In the x-direction, V_{wall} will decrease as the temperature of the solution increases and the vapor-pressure difference decreases. Although it will not be zero at the end of the channel, $\Delta V_x = V_{wall,0}$ is still an appropriate scale factor.

C.3 Scaling the governing equations

The five governing equations are now discussed in turn. Using a short-hand notation for the rest of this analysis, each dimensionless scaled variable (marked with *) is replaced with one, since each of these terms was scaled to be of order one. The magnitude of each of the remaining dimensionless coefficients is then compared with one. To simplify the momentum, energy, and species equations, the following technique is used. First, each equation is divided through by the dominant term that must be retained for the problem to maintain physical significance. The equations are then simplified using the dimensionless numbers from Chapter 4, repeated here in Table C.1.

Dimensionless number	Definition
Reynolds number	$\operatorname{Re} = \frac{U_0 H}{V}$
Wall Reynolds number	$\operatorname{Re}_{wall} = \frac{V_{wall,0}H}{V}$
Thermal Peclet number	$Pe_T = \operatorname{Re}\operatorname{Pr}$
Solutal Peclet number	$Pe_M = \operatorname{Re}\operatorname{Sc}$
Wall thermal Peclet number	$Pe_{wall} = rac{V_{wall,0}H}{lpha}$
Wall solutal Peclet number	$Pe_{M,wall} = rac{V_{wall,0}H}{D_{12}}$
Sparrow number	$Sp = \frac{\dot{q}'''H^2}{k\Delta T_y}$
Thermal Grashof number	$Gr_{\rm T} = \frac{g\beta \ \Delta T_y H^3}{\upsilon^2}$
Solutal Grashof number	$Gr_{\rm M} = \frac{g\beta_M \Delta \omega_y H^3}{v^2}$
Brinkman number	$Br = \frac{\mu U_0^2}{k\Delta T_y}$

Table C.1: Dimensionless numbers used in scaling analysis

C.3.1 Continuity equation

In this short-hand notation, the continuity equation becomes:

$$\frac{\Delta U_x}{x_s} \sim \frac{\Delta V_y}{y_s} \tag{C.26}$$

Using the velocity scales from above gives the axial velocity gradient scale for the x-direction:

$$\Delta U_x \sim \frac{L}{H} V_{wall,0}. \tag{C.27}$$

C.3.2 x-momentum equation

For the x-momentum equation, the dominant term is the transverse viscous term, since this flow is characterized by viscous flow as opposed to inertia flow. This leads to:

$$\frac{U_0 \Delta U_x y_s^2}{\upsilon \Delta U_y x_s} + \frac{V_{wall,0} \Delta U_y y_s^2}{\upsilon \Delta U_y y_s} \sim -\frac{\Delta P_x y_s^2}{\rho \upsilon \Delta U_y x_s} + \upsilon \frac{\Delta U_x y_s^2}{\upsilon \Delta U_y x_s^2} + 1 - \frac{g_x \beta T_s y_s^2}{\upsilon \Delta U_y} - \frac{g_x \beta_M \omega_{l,s} y_s^2}{\upsilon \Delta U_y}$$
(C.28)

Simplifying, rearranging, and replacing the known velocity and length scales gives:

$$\frac{U_0H}{\upsilon} + \frac{V_{wall,0}H}{\upsilon} \sim -\frac{\Delta P_xH^2}{\mu U_0L} + \frac{V_{wall,0}}{U_0}\frac{H}{L} + 1 - \frac{g_x\beta T_sH^3}{\upsilon^2}\frac{\upsilon}{U_0H} - \frac{g_x\beta_M\omega_{1,s}H^3}{\upsilon^2}\frac{\upsilon}{U_0H}$$
(C.29)

Next, since the pressure is also a dominant force in this flow, it should also be of order one. Therefore, the scale for the pressure gradient in the x-direction is:

$$\Delta P_x = \frac{\mu U_0 L}{H^2} \tag{C.30}$$

Note the similarity between this equation and a simple approximation for the pressure drop along the channel:

$$\Delta P_{x} = \mu \frac{\partial u}{\partial y} \bigg|_{y=\pm H} \left(\frac{\text{perimeter}}{\text{area}} \right) = \mu \frac{\partial u}{\partial y} \bigg|_{y=\pm H} \left(\frac{2L}{H} \right)$$
(C.31)

Inserting this into Eq. (C.28) and using the dimensionless numbers from Table C.1 leads to:

$$\operatorname{Re}_{wall} + \operatorname{Re}_{wall} \sim 1 + \frac{\operatorname{Re}_{wall}}{\operatorname{Re}} \frac{H}{L} + 1 - \frac{Gr_T}{\operatorname{Re}} - \frac{Gr_M}{\operatorname{Re}}$$
(C.32)

If these equations are scaled correctly, each of these terms should be on the order of unity or less. If one of the terms is significantly greater than one, then an incorrect scale factor was chosen or this term should have been used to divide through the equation.

C.3.3 y-momentum equation

For the y-momentum equation, two dominant terms are assumed to be the transverse

viscous term and the pressure term. Some further simplification gives:

$$\frac{U_0 H^2}{\upsilon L} + \frac{V_{wall,0} H}{\upsilon} \sim 1 + \frac{V_{wall,0}}{U_0} \frac{H}{L} + 1 - \frac{g_y \beta T_s H^3}{\upsilon^2} \frac{\upsilon}{V_{wall,0} H} - \frac{g_y \beta_M \omega_{1,s} H^3}{\upsilon^2} \frac{\upsilon}{V_{wall,0} H}$$
(C.33)

where the equation was divided through by the transverse viscous term and then the pressure term was set to:

$$\Delta P_{y} = \frac{\mu V_{wall,0}}{H} \tag{C.34}$$

The simplified y-momentum equation is:

$$\operatorname{Re}\frac{H}{L} + \operatorname{Re}_{wall} \sim 1 + \frac{\operatorname{Re}_{wall}}{\operatorname{Re}}\frac{H}{L} + 1 - \frac{Gr_T}{\operatorname{Re}_{wall}} - \frac{Gr_M}{\operatorname{Re}_{wall}}$$
(C.35)

C.3.4 Energy equation

The energy equation is divided through by the transverse conduction term:

$$\frac{U_0 y_T^2}{\alpha L} \frac{\Delta T_x}{\Delta T_y} + \frac{V_{wall,0} y_T}{\alpha} \sim \frac{\Delta T_x y_T^2}{\Delta T_y L^2} + 1 + \frac{y_T^2}{k \Delta T_y} \dot{q}''' + \frac{\mu U_0^2}{k \Delta T_y}$$
(C.36)

where α is the thermal diffusivity. The transverse conduction is balanced by the axial convection which carries the energy along the channel. Therefore, this first term is set to one, which leads to the scale for the y-direction temperature difference:

$$\Delta T_{y} = \frac{U_{0} y_{T}^{2}}{\alpha L} \Delta T_{x}$$
(C.37)

Substituting this into Eq. (C.36) and rearranging gives:

$$1 + \frac{V_{wall,0}y_T}{\alpha} \sim \frac{\alpha}{U_0L} + 1 + \frac{\alpha}{U_0H} \frac{L}{H} \frac{\dot{q}'''H^2}{k\Delta T_x} + \frac{\alpha}{U_0H} \frac{L}{H} \frac{H^2}{y_T^2} \frac{\mu U_0^2}{k\Delta T_x}$$
(C.38)

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Using the dimensionless numbers defined in Table C.1, the final form of the energy equation becomes:

$$1 + \operatorname{Pe}_{wall} \frac{y_T}{H} \sim \frac{1}{\operatorname{Pe}} \frac{H}{L} + 1 + Sp + Br \frac{H^2}{y_T^2}$$
(C.39)

Note that for the energy equation, the y-direction length scale is still undefined. This should be the boundary layer thickness if the flow is still developing or half the channel height (H) if the flow is thermally fully developed. How to choose the appropriate scale is addressed below, but first the species equation is considered in more detail, which is similar to the energy equation.

C.3.5 Species equation

The species equation is divided through by the transverse diffusion term:

$$\frac{U_0 y_M^2}{D_{12}L} \frac{\Delta \omega_{1,x}}{\Delta \omega_{1,y}} + \frac{V_{wall,0} y_M}{D_{12}} \sim \frac{\Delta \omega_{1,x}}{\Delta \omega_{1,y}} \frac{y_M^2}{L^2} + 1$$
(C.40)

and then balance the transverse diffusion with the axial convection of solute, which means that:

$$\Delta \omega_{\mathbf{l},y} = \frac{U_0 y_M^2}{D_{12}L} \Delta \omega_{\mathbf{l},x} \tag{C.41}$$

Substituting this and the dimensionless numbers into Eq. (C.40) leads to:

$$1 + \operatorname{Pe}_{M,wall} \frac{y_M}{H} \sim \frac{1}{\operatorname{Pe}_M} \frac{H}{L} + 1 \tag{C.42}$$

C.3.6 Summary: Non-dimensional, scaled equations

For convenience, the five governing equations are repeated here:

continuity:
$$\frac{\Delta U_x}{L} \sim \frac{\Delta V_y}{H}$$
 (C.43)

x-momentum:
$$\operatorname{Re}_{wall} + \operatorname{Re}_{wall} \sim 1 + \frac{\operatorname{Re}_{wall}}{\operatorname{Re}} \frac{H}{L} + 1 - \frac{Gr_T}{\operatorname{Re}} - \frac{Gr_M}{\operatorname{Re}}$$
 (C.44)

y-momentum:
$$\operatorname{Re} \frac{H}{L} + \operatorname{Re}_{wall} \sim 1 + \frac{\operatorname{Re}_{wall}}{\operatorname{Re}} \frac{H}{L} + 1 - \frac{Gr_T}{\operatorname{Re}_{wall}} - \frac{Gr_M}{\operatorname{Re}_{wall}}$$
 (C.45)

energy:
$$1 + \text{Pe}_{wall} \frac{y_T}{H} \sim \frac{1}{\text{Pe}} \frac{H}{L} + 1 + Sp + Br \frac{H^2}{y_T^2}$$
 (C.46)

species 1:
$$1 + \operatorname{Pe}_{M, wall} \frac{y_M}{H} \sim \frac{1}{\operatorname{Pe}_M} \frac{H}{L} + 1$$
 (C.47)

C.4 Estimating the scale factors

Calculating the terms in Eq. C.43-C.47 requires an estimate for each dimensionless number in Table C.1. The fluid properties in these dimensionless number equations are from Conde [94]. The next few paragraphs estimate the remaining unknown scale factors: y_T , y_M , $V_{wall,o}$, U_o , ΔT_x , $\Delta \omega_x$, and \dot{q}''' .

The length scales x_T and x_M are based on the thermal and species entrance lengths for the channel, which are based on the boundary layer thickness. The thermal boundary layer thickness, as described in Bejan [143], is on the order of:

$$\delta_T \sim \frac{x}{\operatorname{Re}_x^{1/2} \operatorname{Pr}^{1/2}}$$

The value of x where $\delta = H$ (the half-channel height) is the point where the flow becomes fully developed:

$$x_T \sim H \operatorname{Re}_x^{1/2} \operatorname{Pr}^{1/2}$$

Squaring both sides, this becomes:

$$\mathbf{x}_{\mathrm{T}}^{2} \sim H^{2} \operatorname{Re}_{x} \operatorname{Pr} \sim H^{2} \frac{U_{0} \mathbf{x}_{\mathrm{T}}}{v} \operatorname{Pr}$$

Moving the x_T term to the left side, and using the Peclet number (Pe) defined based on the halfchannel heigh (H), the thermal entrance length is:

$$\mathbf{x}_{\mathrm{T}} \sim H \mathbf{P} \mathbf{e}_{\mathrm{T}}$$

Similarly, for the entrance length for the species boundary layer:

$$x_{M} \sim HPe_{M}$$
 (C.49)

The y_T and y_M length scales depend on whether or not the flow is fully developed. If $L > x_T$, then the flow is thermally fully developed and $y_T = H$. Similarly, if $L > x_M$, then the flow is fully developed for species concentration and $y_M = H$. For the heat pump application considered here, the thermal Peclet number is ~10 while the species peclet number is ~10⁴. Assuming that the half-channel height is on the order of 10⁻³, the thermal and species entrance lengths are 0.01 m and 10 m, respectively. Therefore, the y-direction thermal length scale is:

$$y_T \sim H$$

For y_M , the flow is still developing. Therefore, the y-direction length scale for species transfer is the species boundary layer thickness at the end of the channel:

$$y_{\rm M} \sim \frac{H}{{\rm Re}_L^{1/2} \, {\rm Pr}^{1/2}} \sim \frac{L}{P e_{\rm M}}$$
 (C.50)

The wall velocity is estimated based on the modeling from chapter 4. Using typical values from this modeling, an order-of-magnitude wall velocity is:

$$V_{wall,0} \sim 10^{-7}$$

This value is then used to calculate U_0 such that the amount of latent heat transferred to the flow provides enough energy to raise the solution to its maximum possible temperature lift (at an NTU of one):

$$U_{0} \sim \frac{\rho_{w} V_{wall,0} H_{vapor} L}{\rho_{s} c_{p,s} \Delta T_{\max} H}$$
(C.51)

Due to conductive heat losses back to the water side, the x-direction temperature scale will not be the maximum temperature lift, but rather this maximum temperature lift times some effectiveness value:

$$\Delta T_x \sim \mathcal{E}_{lift} \Delta T_{\max} \tag{C.52}$$

A value of 0.6 is used for the temperature-lift effectiveness, which is based on the modeling results from Chapter 5.

The inlet and outlet species mass fractions are based on a species mass balance:

$$(\rho_s U_0 H + \rho_w V_{\text{wall},0} L) \omega_{1,x=L} = \rho_s U_0 H \omega_{1,0}$$

which is modified with some algebra to become the x-direction change in the species mass

fraction (
$$\Delta \omega_{1,x} = \omega_{1,x=L} - \omega_{1,0}$$
):

$$(\rho_s U_0 H + \rho_w V_{\text{wall},0} L) \Delta \omega_x = -\rho_s V_{\text{wall},0} L \omega_0$$

which after some further algebra, becomes:

$$\Delta \omega_{1,x} \sim -\omega_{1,0} \frac{1}{1 + \frac{U_0}{V_{wall,0}} \frac{H}{L}}$$
(C.53)

Since the heat generation due to the enthalpy of mixing occurs inside the species boundary layer, the species boundary thickness is used for the region where the heat of mixing is occurring. The volumetric heat generation is just the total heat generation due to vapor mass flux, divided by this boundary layer thickness:

$$\dot{q}''' \sim \frac{\rho_w V_{wall,0} \Delta H_{mix}}{y_M} \,. \tag{C.54}$$

Nomenclature for Appendix C

Br	Brinkman number
c _p	specific heat capacity (J kg ⁻¹ K ⁻¹)
D_{12}	molecular diffusion coefficient (m ² s ⁻¹)
g	gravity (9.81 m s ⁻²)
Gr	Grashof number based on half channel height
Н	half-channel height (m)
H _{vapor}	enthalpy of water vapor (J kg ⁻¹)
k	thermal conductivity (W $m^{-1} K^{-1}$)
K	mass transfer coefficient (kg m ⁻² s ⁻¹ kPa ⁻¹)
L	channel length (m)
Р	non-hydrostatic pressure (kPa)
p _v	vapor pressure (kPa)
Pe	Peclet number based on half channel height
<i>ġ</i> ‴	heat generation due to heat of mixing (W m^{-3})
Re	Reynolds number based on half channel height
Re _x	Reynolds number based on x-direction distance
Sp	Sparrow number
Т	temperature (K)

U	heat transfer coefficient (W $m^{-2} K^{-1}$)
U ₀	inlet x-direction velocity
u	x-direction velocity (m s^{-1})
V	y-direction velocity (m s ⁻¹)
V _{wall,0}	velocity from the wall (m s^{-1})
х, у	cardinal directions
Greek lette	ers
α	thermal diffusivity $(m^2 s^{-1})$
β_{T}	thermal expansion coefficient (1/K)
β_M	species expansion coefficient (1/K)
δ	boundary layer thickness
ΔT_{lift}	heat pump temperature lift; difference between water and solution temperatures (K)
μ	dynamic viscosity (kg m ⁻¹ s ⁻¹)
ν	kinematic viscosity (m 2 s $^{-1}$)
ω_1	mass fraction of salt, species 1
subscripts	
0	inlet $(x = 0)$; wall location $(y = 0)$
М	term in species (mass fraction) equation
ref	reference value
S	salt solution
Т	term in energy (thermal) equation
W	water
wall	term at the wall; term based on wall velocity

- x x direction
- y y direction

Appendix D

Computational fluid dynamics analysis of boundary-layer flow

This appendix explains the computational fluid dynamics (CFD) analysis of the internal, boundary layer flow. As explained in the scaling analysis in Chapter 4 and in Appendix C, some effects are negligible. This analysis quantifies the effects of three non-negligible terms in the governing equations: (1) the buoyancy in the Navier-Stokes equation due to the density's concentration and temperature dependence, (2) the heat generation from the heat of mixing in the energy equation, rather than including this heat generation in the boundary condition, and (3) the temperature and concentration dependence of the viscosity and diffusion coefficient.

The analysis determines the validity of the assumptions in the simplified finite difference model, where these three effects are ignored. It starts with the base case, which is the same as the numerical model: no natural convection, constant transport properties, heat of mixing generated at the surface of the membrane. It then adds each of these effects separately. Note that there are three natural convection simulations for gravity in the +x, -x, and -y directions, where +x is the direction of flow. Channel symmetry means gravity in the -y and +y directions are the same. Sections D.1 through D.4 explain the process for each simulation, including the mesh, boundary conditions, and calculation and post-processing methods. The results are then presented in Section D.5.

D.1 Model

The considered geometry is a two-dimensional, 0.1-m long channel, as shown in Figure D.1. Three channel thicknesses are considered: 3 mm, 1 mm, and 0.2 mm. The geometry is meshed with quad cells of 0.005 mm height and 0.1 mm length. The mesh includes the entire

channel, rather than just a symmetric half-channel, to capture any natural convection in the ydirection. The boundary conditions are as follows:

- inlet: uniform velocity such that NTU ~ 1.
- outlet: uniform pressure
- membrane surface: robin boundary conditions for heat and mass transfer; velocity through the membrane is set by the mass transfer. These are set using user defined functions, as explained in the next section.



Figure D.1: Geometry and Mesh for boundary layer analysis.

D.2 Membrane boundary conditions

The membrane is assumed to be an impermeable 'wall' in Fluent. In Fluent, a wall must have either a constant surface mass fraction or a zero diffusive flux. Instead, user defined functions simulate the mass transfer by inputting a mass, momentum, and energy source next to the wall. One layer of cells along each wall is placed into a separate zone, with these sources generated in these two zones.



Figure D.2: Boundary conditions for membrane. Heat transfer (q''_{wall}) is to the free-stream temperature (the water flow temperature). Mass transfer (\dot{m}''_{gen}) is a volumetric mass source in the cell, generated based on the difference between the cell's vapor pressure and the free-stream vapor pressure. Associated with the mass source is a momentum source (\vec{p}''_{gen}) and an energy source (\dot{q}''_{gen}) . Equations for each source are in the text.

D.2.1 Mass transfer through the membrane

The mass flux at the wall is based on the difference between the wall-adjacent cell's vapor pressure and the free-stream vapor pressure, which is simply the vapor pressure of the pure water:

$$J_{v} = K_{0} \left(p_{v,w} - p_{v,s} \right)$$
(D.1)

where $p_{v,w}$ is the vapor pressure in the pure water flow on the other side of the membrane and air gap, and $p_{v,s}$ is the vapor pressure of the salt solution next to the membrane. The free-stream vapor pressure is based on the free stream water temperature, which is assumed constant. The water temperature is assumed equal to the solution inlet temperature. The solution vapor pressure is calculated at each wall-adjacent cell as a function of the temperature and concentration in that cell.

The mass transfer coefficient, K_o , is estimated from the numerical model from Chapter 4. It is based on the vapor pressure difference between the membrane-liquid interfaces, which is where the mass flux is generated, as opposed to the vapor pressure difference based on the bulk temperature and concentration. In other words, it does not include temperature or concentration polarization. The free-stream temperature and vapor pressure are assumed constant, with the water at the same temperature as the solution inlet.

The mass flux is converted into a mass source, with units of kg/m³-s, by multiplying by the cell area at the wall (area perpendicular to y direction) and dividing by the total cell volume:

$$\dot{m}_{gen}^{\prime\prime\prime} = \frac{K_0 A_{cell,y} \left(p_{v,w} - p_{v,s} \right)}{V_{cell}} \tag{D.2}$$

This mass source is generated in every cell of the two zones along the top and bottom walls.

There is momentum associated with the mass flux through the wall and this is calculated in a user-defined function with a y-direction momentum source (N/m^3) in the two wall-adjacent zones:

$$\vec{p}_{gen}^{\prime\prime\prime} = \dot{m}^{\prime\prime\prime} v_{wall} \tag{D.3}$$

The y-velocity is the mass flux divided by the density of water:

$$v_{wall} = \frac{J_v}{\rho_w} \,. \tag{D.4}$$

Finally, there is energy generated at the wall-adjacent zones to account for the condensation of water vapor. In the numerical model of Chapter 4, the heat of mixing of the salt solution is generated at the wall along with the heat from condensation. To investigate the validity of this assumption, the energy source is generated with two methods. In the first method (the base case), all of the energy, both condensation and heat of mixing, is generated in the wall-adjacent zones:

$$\dot{q}_{gen}^{\prime\prime\prime} = \dot{m}^{\prime\prime\prime} \left(H_{v} + \Delta H_{mix} \right) \tag{D.5}$$

This method simulates the assumptions made in the numerical model. In the second method, only the heat from condensation is generated in the wall-adjacent zones:

$$\dot{q}_{gen}^{\prime\prime\prime} = \dot{m}^{\prime\prime\prime} H_{\nu} \tag{D.6}$$

with the heat of mixing generated throughout the species boundary layer, as described in Section D.3.

D.2.2 Heat transfer at the membrane

The sensible heat transfer at the membrane surface is simpler to model than the mass transfer. It is modeled with a convection boundary condition:
$$q_{wall}'' = U_0 (T_s - T_w)$$
(D.7)

where U_0 is the overall heat transfer coefficient and T_w is the water temperature. Both U_0 and T_w are assumed constant in this analysis.

D.3 Heat of mixing using a user-defined function

The heat of mixing is calculated based on a species balance for each cell:

$$\rho u A_{cell,y} \omega_s = \left(\rho u A_{cell,y} + \dot{m}_{water}\right) \omega_{s,x+1} \tag{D.8}$$

where ρ is the density of the salt solution, *u* the x-direction velocity, and \dot{m}_{water} the flow rate of 'pure water' entering the control volume, which dilutes the salt solution and releases the heat of mixing. Note that this neglects the y-direction velocity, which is only 0.03% of the x-direction velocity. The water flow rate is used to calculate the heat generated in each cell, and is found by rearranging Eq. (D.8):

$$\dot{m}_{water} = -\frac{\rho u A_{cell,y} \Delta \omega_s}{\omega_s} \tag{D.9}$$

The change in salt mass fraction in this equation is calculated based on the mass fraction gradient of that cell:

$$\Delta \omega_s = \frac{\delta \omega_s}{\delta x} \Delta x \tag{D.10}$$

where Δx is the length of the cell. Finally, the heat of mixing is calculated with:

$$\dot{q}_{gen,mix}^{\prime\prime\prime} = \left| \dot{m}_{water} \Delta H_{mix} \right|. \tag{D.11}$$

D.4 Calculation methods

D.4.1 Settings and assumptions

The model uses a constant mass transfer coefficient, K_0 , of 100 x 10⁻⁶ kg/m²-s-kPa and a constant heat transfer coefficient, U_0 , of 30 W/m²-K. These are based on the assumptions for the membrane in Table 3.4. This mass transfer coefficient gives relatively high mass fluxes (compare to ~40 x 10⁻⁶ kg/m²-s-kPa for the prototype modules), as these will give the largest deviation in temperature and concentration properties, including density, and will give the highest heat generation rate from the enthalpy of mixing.

The mixture properties are based on correlations from Conde [94]. A constant specific heat capacity (2200 J/kg-K) and thermal conductivity (0.56 W/m-K) were assumed, as the scaling analysis in Chapter 4 found little sensitivity to the fluid's thermal properties. User-defined functions are used to calculate the density, viscosity, and diffusivity for each cell in the mesh.

D.4.2 Solution method

The solver uses second-order upwind equations for the spatial discretization of momentum, species, and energy. Although the analysis investigates a steady-state situation, a transient simulation is required for two reasons. First, a transient simulation is required to model natural convection, where the mass inside the fixed-volume domain changes each time step as the density changes with temperature and concentration. The density for the first time step is computed from the initial temperature, so the initial mass is known. As the solution progresses over time, the mass changes so that at the final time step (steady state), the mass is properly conserved. Second, the user-defined functions are based on cell values (density, temperature,

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mass fraction, velocity) from the previous time step to enhance stability and avoid oscillations during successive iterations.

Six simulations were performed on three different geometries, for a total of eighteen simulations. The three geometries use narrow (0.2 mm), moderate (1 mm) and wide (3 mm) channels. The first simulation (the base case) uses constant transport properties, assumes negligible natural convection, and adds the heat of mixing at the membrane surface. The constant transport properties were set at values at the average temperature and concentration. The five remaining simulations investigate, separately, (1) temperature and concentration dependent transport properties, (2-4) the effects of natural convection in the +x, -x, and -y directions), and (5) the effects of distributing the heat of mixing throughout the species boundary layer.

D.4.3 Post processing

Post processing the Fluent results consists of calculating the vapor transfer and calculating the total (latent and sensible) heat transfer to the solution flow. The vapor transfer is calculated by simply subtracting the inlet mass flow rate from the outlet mass flow rate:

$$\dot{m}_{vapor} = \dot{m}_{out} - \dot{m}_{in} \tag{D.12}$$

The total heat transfer is the enthalpy of condensation and the heat of mixing minus the sensible heat transfer back across the membrane. In Fluent, this is calculated with an energy balance between the inlet and outlet flows:

$$q_{total} = \dot{m}_{out}c_p T_{out} - \dot{m}_{in}c_p T_{in}.$$
(D.13)

These two quantities are compared between each of the three simulations to gauge the importance of the assumptions in each case.

D.5 Results

This section presents tabular results for the three geometries for the total energy transfer and total water-vapor transfer to the solution flow. The absolute quantities are not of interest, but rather the ratio of these quantities to those for the base case. Plots are also shown comparing the temperature and velocity profiles for the different cases, when appropriate. The first geometry presented is the thin channel, which has a channel thickness of 0.2 mm (a hydraulic diameter of 0.4 mm). This is close to the geometry of the two hollow fiber prototype designs (inner diameters of 0.28 and 0.33 mm).

D.5.1 0.2-mm channel

Table D.1 shows that for the narrow channel (0.2 mm), small species and temperature gradients make these three effects negligible. Natural convection is insignificant since the density differences, and therefore buoyancy forces, are too small. Temperature and species dependent viscosity and species diffusivity change only minimally, making constant property assumptions reasonable. Finally, the species boundary layer is necessarily thin because of the thin channel (it is fully developed). Therefore, there is little difference between releasing the heat of mixing throughout this boundary layer compared to releasing all of it at the membrane surface.

This analysis confirms that the assumptions used in the simplified finite-difference model are appropriate for the hollow-fiber prototype modules.

		T & ω dependent	dependent natural convection		heat of	
Fluxes	base case	properties	+x	-X	-у	mixing
J_v (g/m ² -s)	0.366	0.366	0.366	0.366	0.366	0.365
q'' (w/m²)	1242	1239	1242	1242	1242	1246
Normalized		T & ω dependent		natural conve	ection	heat of
fluxes	base case	properties	+x	-X	-у	mixing
$J_{_{v}}/J_{_{v,0}}$	1	0.998	1.000	1.000	1.000	0.996
q''/q_0''	1	0.998	1.000	1.000	1.000	1.003

Table D.1: Mass and energy transfers for the 0.2-mm channel. Ratios are relative to the base case.

D.5.2 1-mm channel

The results for the 1-mm channel are shown in Table D.2. The differences between the base case and the other five cases are still small, less than 1% in each case, with the largest difference for the case on the heat of mixing.

Distributing the heat of mixing throughout the species boundary layer affects the shape of the thermal boundary layer, as shown in Figure D.3. Releasing the heat of mixing throughout the species boundary layer, as opposed to all of it at the membrane surface, gives a lower temperature near the wall (view (b)) and a higher temperature near the center of the channel (view (c)). This implies a steeper temperature gradient when releasing all the heat at the membrane surface, and therefore more heat transfer across the membrane. Thus, there is 0.5% more energy transfer for the case with the heat distributed throughout the boundary layer. This effect becomes larger as the species boundary layer thickness increases, as discussed in the next section.

1 dole D.2. Mid	ss and energy	transfers for the f	min channe			le bube euse.
		T & ω dependent		natural conve	ection	heat of
Fluxes	base case	properties	+x	-X	-у	mixing
J_v (g/m ² -s)	0.726	0.726	0.725	0.725	0.726	0.725
<i>q"</i> (w/m²)	3776	3779	3773	3775	3778	3795
Normalized		T & ω dependent		natural conve	ection	heat of
fluxes	base case	properties	$+\mathbf{x}$	-X	-у	mixing
$J_{\nu}/J_{\nu,0}$	1	1.000	0.999	0.999	1.000	0.998
q''/q''_0	1	1.001	0.999	1.000	1.000	1.005

Table D.2: Mass and energy transfers for the 1-mm channel. Ratios are relative to the base case.





Figure D.3: (a) Temperature profile with heat of mixing released at the wall, and heat of mixing distributed throughout species boundary layer. (b) Releasing all the heat of mixing at the membrane surface gives a steeper temperature gradient, and therefore more heat transfer through the membrane. (c) The temperature is higher towards the middle of the channel when the energy is released throughout the temperature boundary layer, rather than at the membrane surface.

D.5.3 3-mm channel

Table D.3 shows the heat and mass fluxes for the 3-mm channel. For this wide channel, natural convection becomes important when gravity is in the same direction as the flow. Due to the large dependence of density on salt mass fraction, the density is 6.5% lower at the wall than at the centerline. Also, for the same mass flow rate (and NTU), the velocity is lower for the wider channel and therefore the ratio of the Rayleigh number to the Reynolds number is higher, indicating natural convection is more relevant.

When gravity is in the opposite direction as the flow, buoyancy forces cause the fluid at the wall to rise more quickly than fluid near the center, leading to the velocity profile in Figure D.4. Also shown is the velocity profile for the cases with no gravity and with gravity in the same

direction as the flow. When the flow is with gravity, the low-density fluid along the wall actually rises next to the high-density fluid in the center. Again, this unusual behavior occurs because the density gradient is very large and the total mass flow rate is small.

For the case when gravity opposes the flow, the higher velocity at the wall more quickly replaces the hot, diluted solution at the wall with more concentrated, colder solution from below. This allows approximately 6% more vapor transfer than the case with no natural convection. When gravity assists the flow, the decreased (and sometimes negative) velocity at the wall limits the heat transfer coefficient there, decreasing the vapor transfer by approximately 2%.

Distributing the heat of mixing also increases the energy flux. It increases by 3.6%, compared to 0.5% for the 1-mm channel. It is not just the larger channel though, it is the species boundary layer thickness that influences the importance of where the heat of mixing energy is released. The species boundary layer at 5 cm (halfway along the channel) was roughly three times thicker (0.6 mm compared to 0.2 mm) for this 3-mm channel than for the 1-mm channel from the previous section.

		T & ω dependent	natural convection			heat of
Fluxes	base case	properties	+x	-X	-у	mixing
J_v (g/m ² -s)	0.626	0.648	0.615	0.662	0.623	0.633
<i>q"</i> (w/m²)	2041	2116	1986	2164	2067	2114
Normalized		T & ω dependent		natural conve	ection	heat of
fluxes	base case	properties	+x	-X	-у	mixing
$J_{_{v}}/J_{_{v,0}}$	1	1.035	0.982	1.057	0.996	1.011
q''/q''_0	1	1 037	0 073	1 060	1 012	1.036

Table D.3: Mass and energy transfers for the 3-mm channel. Ratios are relative to the base case.



Figure D.4: Cross-section velocity profile of 3-mm channel flow with no gravity, gravity against the flow ($g_x = -9.8 \text{ m/s}^2$), and gravity with the flow ($g_x = 9.8 \text{ m/s}^2$).

D.6 Conclusions

The previous CFD simulations show that the model is reasonably accurate for the geometries considered in this thesis. The model can neglect natural convection, use constant transport properties, and add the energy from the heat of mixing at the membrane surface with no effect on the results for the prototype modules.

Only when larger channels are used do these effects become important, primarily because the species boundary layer thickness increases. This boundary layer thickness is not only a function of the channel thickness, but also a function of the salt solution flow rate. More precisely, it is a function of the species Peclet number, as defined in the scaling analysis in Chapter 4. A larger species boundary layer thickness means larger concentration differences, and therefore larger differences in transport properties and density. The larger difference in transport properties makes a constant-property assumption less accurate, and the larger density difference leads to natural convection. A larger species boundary layer also increases the difference between modeling the release of the heat of mixing at the membrane surface and modeling it throughout the species boundary layer.

Modelers should take care of modeling larger channel thicknesses with the model used in this thesis, as the effects of natural convection and heat generation become more important.

Nomenclature for Appendix D

$A_{y,cell}$	area of finite-volume cell, perpendicular to y direction (m^2)
c _p	specific heat capacity (J kg ⁻¹ K ⁻¹)
H _{vapor}	enthalpy of water vapor (J kg ⁻¹)
J_{v}	vapor flux (kg m ⁻² s ⁻¹)
K_0	mass transfer coefficient neglecting polarization (kg m ⁻² s ⁻¹ kPa ⁻¹)
L	channel length (m)
ṁ	mass flow rate (kg s ⁻¹)
<i>ṁ</i> ‴	volumetric mass generation (kg $m^{-3} s^{-1}$)
Р	non-hydrostatic pressure (kPa)
\vec{p}'''_{gen}	volumetric momentum generation (N m ⁻³)
$p_{\rm v}$	vapor pressure (kPa)
q	heat transfer rate (W)

q''	heat flux	(W	m^{-2})
1		· ·	

$\dot{q}'''_{gen,mix}$	volumetric heat generation due to heat of mixing (W m ⁻³)
Т	temperature (K)
U_0	heat transfer coefficient neglecting polarization (W $m^{-2} K^{-1}$); inlet x-velocity (m s^{-1})
u	x-direction velocity (m s^{-1})
v	y-direction velocity (m s ⁻¹)
V _{cell}	volume of finite-volume cell (m ³)
V _{wall}	y-direction velocity at the wall due to mass generation at the wall (m s^{-1})
C	

Greek letters

ΔH_{mix}	heat of mixing (J kg ⁻¹)
ρ	density (kg m ⁻³)

 $\omega_s \qquad \text{mass fraction of salt}$

subscripts

0	base-case value
in	inlet value to a cell
out	outlet value from a cell
S	salt solution
W	water
wall	term at the wall; term based on wall velocity
X	x direction
<i>x</i> +1	cell adjacent to cell <i>x</i>
У	y direction

Appendix E Uncertainty analysis

This appendix presents the uncertainty analyses for both the model and the experiments.

E.1 Modeling uncertainty

Table E.1 shows the independent variables for the finite difference model along with their uncertainties. These were determined as follows. The membrane porosity, tortuosity, and pore size were estimated with the techniques in Chapter 3, with uncertainties quantified from these measurements. The inner and outer diameters of the hollow fibers were measured with SEM images of the fibers after breaking them in liquid nitrogen, with uncertainties from repeated measurements on different fibers. The gap width and its uncertainty are from the manufacturer, Applied Membrane Technology, Inc. Note that this gap width is the thickness of the plastic spacer separating each row and therefore it is the distance between the outer surfaces of the hollow fibers. Finally, the uncertainty in the Nusselt and Sherwood numbers are from scaling analyses discussed in Chapter 4. The uncertainties in solution transport properties (viscosity, diffusivity, and thermal conductivity) are included in the uncertainties of the Nusselt and Sherwood numbers.

Variable (units)	Symbol	Measured value, X	Uncertainty, u _X	Percent uncertainty, %ux
Inner diamter (m)	d_i	0.00028	0.000005	2%
Outer diameter (m)	d _o	0.00038	0.000005	1%
Gap width (m)	d_{gap}	0.00091	0.000075	8%
Porosity	3	0.43	0.02	5%
Pore size (m)	d _p	6.20E-08	6.00E-09	10%
Tortuosity	τ	5.6	0.5	9%
Nusselt number	Nu	4	1	25%
Sherwood number	Sh	4	1	25%

Table E.1: Independent variables, their values, and their uncertainties

The uncertainties in Table E.1 must be propagated through to the three dependent variables: the temperature lift (ΔT_{lift}), the overall mass transfer coefficient (K), and the overall heat transfer coefficient (U). The analysis first calculates the partial derivatives of the three performance metrics with respect to each of these independent variables. These are calculated numerically with an iteration procedure in the Engineering Equation Solver (EES) program. Each partial derivative is shown in Table E.2 for a 0.91 mm air gap (the largest gap width prototype) and Table E.2 for a 0.56 mm gap (the smallest gap width prototype). Also shown is a sensitivity coefficient, which is the percentage of the overall uncertainty in each dependent variable attributable to each independent variable.

For both the small and large air gap width modules, some general conclusions can be drawn. The membrane parameters (pore size, porosity, tortuosity) account for 91% of the mass transfer coefficient uncertainty. The membrane parameters have little effect on the overall heat transfer coefficient, where they account for less than 1%. The uncertainty in the air gap width dominates; it accounts for more than 99% of the heat transfer coefficient uncertainty. For the temperature lift, the uncertainties in both the membrane parameters and the air gap are important. For all of the dependent variables, the uncertainties in the fiber diameters contribute a small amount, and the Nusselt and Sherwood number uncertainties are negligible.

The propagated uncertainties for these two cases are shown in Table E.4. Note that the transport coefficient uncertainties are shown as a percent, while the temperature lift is shown in degrees C.

-	-		01				
Variable	dK/dX	dU/dX	$\Delta T_{lift}/dX$		S _{K-X}	S_{U-X}	$S_{\Delta T-X}$
di	370600	38456	42066		5.1%	0.3%	4.5%
d _o	-272900	-8395	-32624		2.8%	0.0%	2.7%
$\mathbf{d}_{\mathrm{gap}}$	-6762	-37881	2295		0.7%	99.1%	5.3%
3	73.61	-0.3363	9.016		12.9%	0.0%	13.1%
d _p	3.71E+08	1.57E+07	4.41E+07		29.5%	0.2%	28.2%
τ	-5.735	-0.2427	-0.676		48.9%	0.4%	46.1%
Nu	7.19E-03	-0.02097	0.002616		0.0%	0.0%	0.0%
Sh	1.15E-01	-0.01848	0.0156		0.1%	0.0%	0.1%
				$\sum =$	100.0%	100.0%	100.0%

Table E.2: Partial derivatives and the sensitivity coefficient of the three dependent variables with respect to the independent variables. $d_{gap} = 0.91 \text{ mm}$

Table E.3: Partial derivatives and the sensitivity coefficient of the three dependent variables with respect to the independent variables. $d_{gap} = 0.56 \text{ mm}$

Variable	dK/dX	dU/dX	$\Delta T_{\text{lift}}/dX$		S_{K-X}	S_{U-X}	$S_{\Delta T-X}$
d_i	420300	67787	37883		5.2%	0.1%	3.8%
d _o	-309400	-27734	-29020		2.8%	0.0%	2.2%
d_{gap}	-8179	-91802	3889		0.8%	99.7%	16.1%
3	83.42	-3.895	8.408		13.1%	0.0%	12.1%
d _p	4.2E+08	1.81E+07	4.04E+07		29.8%	0.1%	25.1%
τ	-6.42	-0.2775	-0.6172		48.3%	0.1%	40.6%
Nu	5.18E-03	-0.02226	0.001674		0.0%	0.0%	0.0%
Sh	1.28E-01	-0.03248	0.01423		0.1%	0.0%	0.1%
				$\sum =$	100.0%	100.0%	100.0%

Table E.4: Propagated uncertainties from independent variables to temperature lift and overall mass and heat transfer coefficients.

Gap width	$\% u_{\rm K}$	$\% u_{\rm U}$	$u_{\Delta T}(^{o}C)$
d _{gap} = .91 mm	9.0%	4.6%	0.48
d _{gap} = .56 mm	10.4%	7.4%	0.48

E.2 Experimental uncertainty

The uncertainties in the measured parameters are shown in Table E.5. As in the model uncertainty analysis, the partial derivatives are calculated for the three performance metrics with respect to each measured variable. These are again calculated numerically with an iteration procedure in the EES program. As shown in Table E.6, the salt mass fraction measurement and the vapor flux measurement contribute the most to the uncertainty in the overall mass transfer coefficient. The overall heat transfer coefficient is also sensitive to the uncertainty in the vapor flux measurement, but the temperature measurements also are important. The simplicity of the temperature lift equation means that there are only two temperature measurements that contribute to its uncertainty. The same conclusions can be drawn for the sensitivity coefficients in Table E.7, which are for CaCl₂ instead of LiCl. Table E.8 shows the propagated uncertainties to the three dependent variables. The uncertainties for CaCl₂ are higher for the two transport coefficients due to the smaller value of the vapor flow rate, and therefore larger percent uncertainty. The temperature lift uncertainties are the same, as these depend only on temperature measurements.

Variable (units)	Symbol	Measured value, X	Uncertainty, u _X	Percent uncertainty, %ux
Exchange area (m ²)	A _{ex}	0.25	0.0025	1%
Solution flow rate (g/s)	\dot{m}_s	0.57-1.3	0.05	4-9%
Vapor flow rate (g/s)	$\dot{m}_{_{vapor}}$	0.01025	0.0005	2%-5%
Water flow rate (g/s)	$\dot{m}_{_{W}}$	0.26-3.5	0.05	1.5-20%
Temperatures (°C)	T_i	15-45	0.1	n/a
Mass fraction (-)	ω _s	0.3-0.39	0.005	13-17%

Table E.5: Measured parameters and uncertainties for heat pump experiments

1	1					
Variable	dK/dX	dU/dX	$\Delta T_{lift}/dX$	S_{K-X}	$\mathbf{S}_{\mathrm{U-X}}$	$S_{\Delta T-X}$
A _{ex}	-157.6	-219.1	0	6.8%	2.6%	0.0%
m _s	-0.7266	-10.924	0	0.1%	2.7%	0.0%
m _{vapor}	2049	3945	0	47.0%	35.1%	0.0%
m _w	-1.167E-13	-3.236	0	0.0%	0.2%	0.0%
T _{s,in}	0.6331	-7.891	0	0.2%	5.6%	0.0%
T _{s_out}	0.95	-12.283	1	0.4%	13.6%	50.0%
$T_{w,in}$	-2.059	-0.8411	-1	1.9%	0.1%	50.0%
T _{w,out}	-1.787	21.06	0	1.4%	39.9%	0.0%
ω _s	-194.3	31.31	0	42.2%	0.2%	0.0%
				$\Sigma = 100\%$	100%	100%

Table E.6: Partial derivatives and the sensitivity coefficient of the three dependent variables with respect to the independent variables. LiCl as desiccant.

Table E.7: Partial derivatives and the sensitivity coefficient of the three dependent variables with respect to the independent variables. $CaCl_2$ as desiccant

Variable	dK/dX	dU/dX	∆Tlift/dX	S_{K-X}	$\mathbf{S}_{\mathrm{U-X}}$	$\mathbf{S}_{\Delta T-\mathbf{X}}$
A _{ex}	-175.1	-271.2	0	2.02%	0.76%	0.00%
ms	-0.9493	-9.714	0	0.00%	0.04%	0.00%
m _{vapor}	4891	8939	0	64.17%	33.72%	0.00%
m _w	0.002479	-2.995	0	0.00%	0.04%	0.00%
T _{s,in}	2.479	-25.58	0	0.66%	11.05%	0.00%
T _{s_out}	3.245	-32.463	1	1.13%	17.79%	50.00%
$T_{w,in}$	-4.479	13.56	-1	2.15%	3.10%	50.00%
T _{w,out}	-3.79	44.54	0	1.54%	33.49%	0.00%
ω _s	-321.4	18.13	0	28.32%	0.01%	0.00%
				$\sum = 100\%$	100%	100%

Table E.8: Propagated uncertainties from independent variables to temperature lift and overall mass and heat transfer coefficients.

Desiccant	$\% u_{\rm K}$	$\% u_{\rm U}$	$u_{\Delta T}(^{o}C)$
LiCl	3.5%	5.5%	0.14
CaCl ₂	6%	10.7%	0.14