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THERMODYNAMIC PROPERTIES OF LITHIUM BROMIDE/WATER SOLUTIONS WITH APPLICATION TO AN ABSORPTION TEMPERATURE BOOSTING HEAT PUMP

The Ohio State University

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Thermodynamic Properties of Lithium Bromide/Water Solutions With Application to an Absorption Temperature Boosting Heat Pump

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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The Ohio State University 1985

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LIST OF NOMENCLATURE

ROMAN

$a_f$ - flow availability

$a$ - activity

$\Lambda_{DH}$ - Debye-Huckel constant

$B$ - Pitzer constant

$c_p$ - isobaric specific heat

$c_v$ - isochoric specific heat

$C, D, E$ - Pitzer constants which become functions of temperature and pressure in the present study

$C_i, D_i, E_i$ - Constants for $i=1, \ldots, 10$

$e^0$ - fundamental electric charge

$E$ - total energy

$f_p$ - fugacity

$g$ - specific Gibbs free energy

$G$ - Gibbs free energy

$h$ - specific enthalpy

$H$ - enthalpy

$I$ - integration function

$I$ - irreversibility rate

$k_A$ - Boltzmann's constant

$k_i$ - constants for $i=1, \ldots, 4$
- dimensionless constants for i=1,...,4
- constants for i=1,...,3
- dimensionless constants for i=1,...,3
- length
- dimensionless molality
- mass flow rate
- conventional molality
- molecular weight
- number of moles
- moles of solvent per kg of solvent
- total number of data points
- Avogadro's number
- pressure
- component pressure of component i
- heat transfer
- heat transfer rate
- gas constant
- squared multiple correlation coefficient
- specific entropy
- entropy
- temperature
- specific internal energy
- internal energy
- specific volume
- partial molal volume of component i
$V$  - volume
$w$  - data weight
$W$  - work
$X$  - mole fraction
$X_m$  - mass fraction
$y_i$  - undetermined constants

GREEK

$\alpha$  - Pitzer constant
$\Delta$  - denotes a difference
$\varepsilon_{\varepsilon}$  - dielectric constant of water
$\varepsilon_0$  - permittivity of free space
$\varepsilon$  - second law performance measure
$\phi$  - sum of the squared residuals
$\phi_p$  - osmotic coefficient
$\gamma$  - activity coefficient
$\eta$  - first law performance measure
$\lambda$  - the mass fraction of water in the standard state
$\mu$  - chemical potential
$\pi$  - dimensionless pressure
$\theta$  - dimensionless temperature
$\rho$  - density
$\sigma$  - standard deviation
$\dot{\sigma}$  - entropy production rate
$\Omega$  - generic thermodynamic property
ψ  - specific Helmholtz free energy
Ψ  - Helmholtz free energy

SUBSCRIPTS

alt  - alternate form
A    - absorber
C    - condenser
CD   - terms involving C and D
e    - exit
ex   - excess property
E    - evaporator
G    - generator
H    - recuperative heat exchanger
i    - inlet
int. rev. - internally reversible
I    - intermediate value
L    - loss
0    - reference state
PDH  - Pitzer Debye-Huckel term
R    - dimensionless quantity
RMS  - root mean squared quantity
rel  - relative value
RCX  - dimensionless term involving C with composition dependence factored out
s    - reference property
T    - throttling model
\( t \) - mean value

**SUPERSCRIPTS**

\( ^o \) - standard state

\( ^* \) - ideal model

**MISCELLANEOUS SYMBOLS**

\( . \) - a dot above a symbol denotes a rate quantity

\( \mathcal{d} \) - inexact differential

\( \equiv \) - denotes a definition

\( \rightarrow \) - denotes a range of values
The investigation reported here concerns mainly the thermodynamic properties of LiBr/H₂O solutions relevant to absorption chillers and heat pumps.

At the outset of the present study, efforts to quantify the thermodynamic performance of absorption cycles were hindered by a lack of consistent enthalpy and entropy data on the absorption pair, LiBr/H₂O. Accordingly, the principal objective of this investigation is the generation of an analytic Gibbs free energy surface for LiBr/H₂O from which accurate values of thermodynamic properties can be readily calculated. The versatility of the Gibbs free energy surface in calculating consistent and accurate thermodynamic properties over the entire range of the independent variables relevant to absorption system analysis makes it a significant new tool in the analysis of absorption systems.

The Gibbs free energy expression yields the specific enthalpy and entropy values required for first and second law analyses of the components of an innovative absorption cycle known as a temperature
boosting heat pump cycle. These analyses provide both a quantitative evaluation of the sources of irreversibility and a refined understanding of the practical potential of the cycle.
Chapter 1

Fundamental Thermodynamic Concepts

The purpose of this presentation of fundamentals is to define the thermodynamic variables and concepts which will be combined later into a description of the thermodynamics of absorption working pairs. Readers who are well versed in the thermodynamics of binary component systems may want to proceed directly to Section 1.4. The notation system used throughout the present study is introduced in the present chapter in familiar defining relations. This will allow later developments to focus on the special aspects of absorption pair thermodynamics. A more detailed treatment of fundamentals can be found in the literature references [24,27].

1.1 Closed Systems of Fixed Composition

An expression of the First Law of Thermodynamics in differential form for closed systems is,

\[ dE = dq - dw \]  

(1.1)
where it has been assumed that the heat transfer, $Q$, is positive when flowing into the system and the work, $W$, is positive when it is being done by the system.

In Eq. 1.1, $E$ denotes the total energy of the system. In many systems of interest, the internal energy, $U$, is the only component of the total energy which undergoes significant changes. In other words, changes in kinetic and potential energy of the system are negligible. This will be assumed throughout the ensuing development. Accordingly, the Eq. 1.1 can be written in differential form as

$$dU = dQ - dW \quad (1.2)$$

Boundary work effects ("pdV" work) must be considered if the system boundaries are not fixed. Simple compressible systems are defined as those systems which experience only "pdV" work while undergoing quasistatic (internally reversible) processes. For such systems,

$$(dW)_{\text{int rev}} = pdV \quad (1.3)$$

All of the systems which will be considered in this work are simple compressible systems.

An expression of the Second Law of Thermodynamics
in differential form for a closed system undergoing an internally reversible process is,

\[ dS = \frac{dQ}{T} \]  

(1.4)

Equation 1.4 is the defining relation for the entropy, \( S \), of the system.

Combining Eqs. 1.2, 1.3 and 1.4 results in,

\[ TdS = dU + pdV \]  

(1.5)

This relation is of fundamental importance in classical thermodynamics because it relates changes in the properties of a simple compressible system of fixed composition in such a way that a large body of relationships between properties can be developed [24]. The relationships presented next are useful in subsequent developments.

The enthalpy, \( H \), the Helmholtz free energy, \( \Psi \), and the Gibbs free energy, \( G \), are defined as follows.

\[ H = U + pV \]  

(1.6)

\[ \Psi = U - TS \]  

(1.7)

\[ G = H - TS \]  

(1.8)

Differentiation of Eqs. 1.6 to 1.8, respectively, and substitution of Eq. 1.5 yields,
\[
dH = TdS + Vdp \quad (1.9)
\]
\[
d\Psi = -pdV - SdT \quad (1.10)
\]
\[
dG = Vdp - SdT \quad (1.11)
\]
\[
dU = TdS - pdV \quad (1.5)
\]

where Eq. 1.5 has been included to complete the set of differential relations.

Equations 1.5 and 1.9 to 1.11 emphasize that for a simple compressible, closed system of fixed composition there are at most two independent thermodynamic variables of state. That is, the following functional forms are suggested by these equations.

\[
U = U(S,V) \quad (1.12)
\]
\[
H = H(S,p) \quad (1.13)
\]
\[
\Psi = \Psi(V,T) \quad (1.14)
\]
\[
G = G(T,p) \quad (1.15)
\]

The total differential of the foregoing functions can be written as,

\[
dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \quad (1.16)
\]
\[ \text{d}H = \frac{\partial H}{\partial S} \text{d}S + \frac{\partial H}{\partial p} \text{d}p \quad (1.17) \]

\[ \text{d}U = \frac{\partial U}{\partial V} \text{d}V + \frac{\partial U}{\partial S} \text{d}S \quad (1.18) \]

\[ \text{d}G = \frac{\partial G}{\partial T} \text{d}T + \frac{\partial G}{\partial p} \text{d}p \quad (1.19) \]

Comparison of Eqs. 1.5 and 1.9 to 1.11 with Eqs. 1.16 to 1.19 yields the following relations.

\[ \frac{\partial U}{\partial S} V = T \quad (1.20) \]

\[ \frac{\partial U}{\partial V} S = -p \quad (1.21) \]

\[ \frac{\partial H}{\partial S} P = T \quad (1.22) \]

\[ \frac{\partial H}{\partial p} S = V \quad (1.23) \]

\[ \frac{\partial U}{\partial T} T = -p \quad (1.24) \]

\[ \frac{\partial U}{\partial V} V = -S \quad (1.25) \]
(1.26)

\[ \frac{\partial G}{\partial T} = -S \]

(1.27)

\[ \frac{\partial G}{\partial p} = V \]

Furthermore, a set of relations known as Maxwell Relations may be obtained by an application of the test for exactness [25] to the total differentials in Eqs. 1.16 to 1.19. These relations are as follows.

(1.28)

\[ \frac{\partial T}{\partial S} = -\frac{\partial p}{\partial V} \]

(1.29)

\[ \frac{\partial T}{\partial p} = \frac{\partial V}{\partial S} \]

(1.30)

\[ \frac{\partial p}{\partial V} = \frac{\partial S}{\partial T} \]

(1.31)

\[ \frac{\partial V}{\partial p} = -\frac{\partial S}{\partial T} \]

For many applications it is convenient to consider thermodynamic properties on a unit mass or intensive (see Glossary) basis. An intensive form for each of the extensive (see Glossary) thermodynamic properties considered can be obtained by dividing the extensive
property by the amount of mass in the system under consideration. Corresponding extensive and intensive properties are denoted respectively by upper and lower case symbols. All of the previously obtained results can be written in terms of intensive properties by considering the closed system under study as consisting of a unit mass.

The specific heats on an intensive basis are

\[ c_v = \frac{\partial u}{\partial T}, \quad c_p = \frac{\partial h}{\partial T} \]  

(1.32)  

(1.33)

The definitions and derived relations given above allow the following expressions for the differentials of the thermodynamic properties to be derived [24].

\[ du = c_v dT + \left( T(\partial) + p \right) dv \]  

(1.34)

\[ dh = c_p dT + (v - T(\partial) p) dp \]  

(1.35)

\[ d\psi = -pdv - sdT \]  

(1.36)

\[ dg = vdp - sdT \]  

(1.37)
\[
\frac{\partial v}{\partial T} = \frac{\partial v}{\partial p}
\]

These relations enable values of the thermodynamic properties of a pure substance to be calculated from measurements of \(p, T, v, c_v\) and \(c_p\), all of which can be readily determined experimentally. Thus Eqs. 1.34 to 1.38 provide the link between these readily measurable properties and the intensive properties \(u, h, \psi, g\) and \(s\). The ability to obtain a thermodynamic property of interest from measured data represents a key step in the application of thermodynamics to practical problems.

This completes an overview of property relations for simple compressible, closed systems of fixed composition. A discussion of property relations for binary component systems is presented next.

1.2 Binary Component System Analysis

The fluids circulating inside absorption chillers and heat pumps are binary solutions (see Glossary). Accordingly, the topic of thermodynamic properties of binary solutions is fundamental to the present study and is discussed in this section. However, before developing property relationships for binary systems, a
brief preview of the eventual application of this material, discussed in detail in Chapter 6, is presented.

1.2.1 Application Preview

Two absorption working pairs are in common use in absorption chillers and heat pumps: LiBr/H$_2$O and H$_2$O/NH$_3$. Each pair is designated in the format: absorbent/refrigerant. Note that H$_2$O plays the role of the refrigerant in the pair LiBr/H$_2$O and the absorbent in the pair H$_2$O/NH$_3$. In an absorption cycle, the absorbent and the refrigerant are separated in one component and reunited as a solution in another component. The thermodynamic properties of the binary component working pairs determine the energy flows necessary to drive these processes in an absorption cycle.

Both of the absorbent/refrigerant working pairs mentioned here are utilized in practical cycles because they possess a wide range of advantages [6] such as high mutual solubility, low viscosity, low absorbent volatility and high refrigerant volatility. Of particular significance are the vapor/liquid equilibrium characteristics of each of these pairs. The following description of the vapor/liquid characteristics of each
pair will emphasize the significant differences between the pairs. However, the feature which makes each useful as an absorption working pair is the relative ease with which the refrigerant can be separated from the absorbent.

Water/ammonia absorption systems are characterized by the need for special components designed to remove the absorbent (H\textsubscript{2}O) from the refrigerant (NH\textsubscript{3}) vapor. A small but significant portion of the absorbent vaporizes along with the refrigerant when the solution is boiled. As an example, NH\textsubscript{3} and H\textsubscript{2}O exist as a two phase system (vapor/liquid) at 120°C and 35 bar. The equilibrium composition of the liquid phase is 50% NH\textsubscript{3} by mass. The equilibrium vapor composition is 95.76% NH\textsubscript{3} by mass. Thus if these conditions exist in the generator, the vapor produced contains 4.24% H\textsubscript{2}O by mass. This apparently small presence of H\textsubscript{2}O in the vapor has a significant effect on the cycle unless it is removed by a special component commonly called a rectifier.

Lithium bromide/water absorption systems are significantly different than H\textsubscript{2}O/NH\textsubscript{3} systems. In LiBr/H\textsubscript{2}O systems, the vapor/liquid phase equilibrium characteristics are such that the vapor is effectively pure H\textsubscript{2}O at conditions encountered in typical cycles. The presence of LiBr in the vapor is so diffuse that it
is difficult to measure. As an example, a LiBr/H₂O system exists in vapor/liquid equilibrium at 120°C and 0.6 bar. The equilibrium composition of the liquid phase is 50% LiBr by mass while the vapor is effectively pure H₂O.

This brief sketch of absorption systems foreshadows the cycle analysis work discussed in Chapter 6. The goal of its inclusion here is to motivate the detailed discussion of binary system thermodynamics which follows immediately.

1.2.2 Chemical Potential, Fugacity and Activity

In this discussion, attention will be focused on simple compressible, binary component systems. These are systems which contain two components and which experience only "pdV" work while undergoing quasistatic processes. The state of such a system is completely determined by the amount of each component plus two independent properties. The chemical potential is introduced to facilitate the analysis of such systems. Two properties related to the chemical potential, the fugacity and the activity, are also introduced. An understanding of the chemical potential concept is a key to taking thermodynamics beyond fixed composition considerations.
1.2.2.1 Chemical Potential

For a system of 2 components, the thermodynamic properties internal energy, enthalpy, Helmholtz free energy and Gibbs free energy can be expressed as follows.

\[ U = U(S, V, n_1, n_2) \] (1.39)

\[ H = H(S, p, n_1, n_2) \] (1.40)

\[ \psi = \psi(T, V, n_1, n_2) \] (1.41)

\[ G = G(T, p, n_1, n_2) \] (1.42)

where \( n_i \) represents the number of moles of the \( i^{th} \) component.

The total differentials of these functions can be written as

\[
\begin{align*}
\text{d}U &= T\text{d}S - pdV + \frac{\partial U}{\partial n_1}dn_1 + \frac{\partial U}{\partial n_2}dn_2 \\
\text{d}H &= T\text{d}S + Vdp + \frac{\partial H}{\partial n_1}dn_1 + \frac{\partial H}{\partial n_2}dn_2 \\
\text{d}\psi &= -pdV - SdT + \frac{\partial \psi}{\partial n_1}dn_1 + \frac{\partial \psi}{\partial n_2}dn_2
\end{align*}
\] (1.43-1.45)
\[ dG = Vdp - SdT + \left( \frac{\partial G}{\partial n_1} \right)_{p,T,n_2} \, dn_1 + \left( \frac{\partial G}{\partial n_2} \right)_{p,T,n_1} \, dn_2 \]  

(1.46)

By definition, the partial molal forms of an extensive property \( Y(T,p,n_1,n_2) \) are \( \frac{\partial Y}{\partial n_1} \) and \( \frac{\partial Y}{\partial n_2} \). Thus, the partial derivatives in Eq. 1.46 are known as the partial molal Gibbs free energies of the components. Note that the derivatives in Eqs. 1.43 to 1.45 do not represent partial molal properties. The partial molal Gibbs free energy of a component is often referred to as the chemical potential of the component. This terminology is formalized in the following definition of the chemical potential of component \( i \), denoted \( \mu_i \).

\[ \mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_{j\neq i}} \]  

(1.47)

Substitution of the definitions of the enthalpy and the Gibbs and Helmholtz free energies (Eqs. 1.6 to 1.8) into the expressions in Eqs. 1.43 to 1.46 yields the following relationships after some rearrangement.

\[ \mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S,V,n_{j\neq i}} = \left( \frac{\partial H}{\partial n_i} \right)_{S,p,n_{j\neq i}} = \left( \frac{\partial Y}{\partial n_i} \right)_{V,T,n_{j\neq i}} \]  

(1.48)

Using the chemical potential, Eqs. 1.34 to 1.38 can be extended to binary component systems as follows.
\[ du = c_v \frac{\partial p}{\partial T} + \{T(--) \frac{\partial \nu}{\partial T} \nu, \beta, \rho \} d\nu + \frac{\mu_1 dX_1}{X_2} + \frac{\mu_2 dX_2}{X_1} \quad (1.49) \]

\[ dh = c_p dT + \{v - T(--) \frac{\partial \nu}{\partial T} \nu, \beta, \rho \} dp + \frac{\mu_1 dX_1}{X_2} + \frac{\mu_2 dX_2}{X_1} \quad (1.50) \]

\[ d\psi = -pd\nu - s dT + \frac{\mu_1 dX_1}{X_2} + \frac{\mu_2 dX_2}{X_1} \quad (1.51) \]

\[ dg = v dp - s dT + \frac{\mu_1 dX_1}{X_2} + \frac{\mu_2 dX_2}{X_1} \quad (1.52) \]

\[ ds = \frac{c_v dT}{T} - \{-- \} \frac{\partial \nu}{\partial T} \nu, \beta, \rho \} dp + \frac{\mu_1 dX_1}{TX_2} + \frac{\mu_2 dX_2}{TX_1} \quad (1.53) \]

Where \( X_i \) is the mole fraction of component \( i \), defined as

\[ X_i = \frac{n_i}{n_1 + n_2} \quad (1.54) \]

A related composition measure which is in common use is the mass fraction, \( X_m \), defined as

\[ X_m = \frac{n_i M_i}{n_1 M_1 + n_2 M_2} \quad (1.55) \]

The set of equations including Eqs. 1.49 to 1.53 describe the variation of the thermodynamic properties \( u, h, \psi, g \) and \( s \) in terms of the chemical potentials,
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μ_i, and a set of readily measurable properties (c_v, c_p, T, p, v, X_i). The methods available for calculating values of the chemical potential from experimental data are quite complex. One such method, called the free energy surface method, is used in the present study. A description of this method is presented in Section 1.4. The next topic considered is the fugacity, which is required for subsequent discussions.

1.2.2.2 Fugacity and Activity

The relationship of the chemical potential to measurable properties is complex. Some simplification can be obtained by introducing a related property called the fugacity. The fugacity, which has dimensions of pressure, was first introduced by Lewis [28]. The fugacity is defined next for a gaseous solution.

The fugacity of a component in a gaseous solution, denoted f_i, is defined as follows

\[ \frac{d(\ln f_i)_T}{RT} = -\frac{1}{RT}d(\mu_i)_T \]  

(1.56)

with the additional requirement that

\[ \lim_{p \to 0} \frac{f_i}{p_i} = 1 \]  

(1.57)
where,

\[ p_i \] - component pressure of component \( i \) (see Glossary)

\[ R \] - gas constant

Because this definition applies only for the case of a gaseous system, the fugacity of a component in other phases of matter must be deduced with additional information (see [24,27]). The relationship between the values of the fugacity of a component in each of two phases at equilibrium is the key to evaluating the fugacity of a component in a liquid or solid phase. The general topic of phase equilibrium is discussed in the next section (Section 1.2.2).

The fugacity is related to measurable quantities by the following equation which applies to gaseous solutions at constant temperature and composition. A derivation of this equation can be found in [24]. For component \( i \),

\[
\ln f_i = \ln p_i + \frac{p}{RT} \int_0^\pi \left[ \frac{v_i}{\pi} - \frac{1}{\pi^2} \right] d\pi
\]  \hspace{1cm} (1.58)

where \( v_i \) is the partial molal volume of component \( i \) and \( \pi \) is a dummy integration variable. Thus, if sufficient volumetric data are available, the fugacity can be directly calculated. The fugacity is a convenient means for reproducing the pressure and composition dependence of the chemical potential.
In practical applications it is usually more convenient to deal with the ratio of the fugacity to the fugacity in some standard state. This "relative fugacity" is called the activity, \( a_i \).

\[
a_i = \frac{f_i}{f_i^*}
\]

Where

\( a_i \) - activity of component \( i \)

\( f_i \) - fugacity of component \( i \)

\( f_i^* \) - fugacity of component \( i \) in some specified standard state

Introduction of the activity leads to the following simple expression for the chemical potential

\[
\mu_i = \mu_i^* + RT \ln a_i
\]

The standard state, denoted by superscript \( o \), may be chosen arbitrarily. However, practice has introduced useful conventions to guide the selection. In particular, the conventional choice will depend on the specific substances involved [24]. Careful specification of the standard state in use will be made whenever the activity is utilized in the following discussion.

It is also conventional to define an activity coefficient, \( \gamma_i \), as
where

\[ \gamma_i = \frac{a_i}{X_i} \]

\[ (1.61) \]

\( \gamma_i \) - activity coefficient of component \( i \)

\( a_i \) - activity of component \( i \)

\( X_i \) - mole fraction of component \( i \)

In this definition, the mole fraction of component \( i \) has been used as the composition measure. Frequently, other composition measures are used in place of the mole fraction. Activity coefficients based on different composition measures will, in general, have different values at a given state. Care is taken in this work to clearly define the activity coefficient in each development which utilizes this quantity.

Activity coefficients represent the deviation of the activity from the composition measure. It is useful to view the activity coefficient as a measure of the deviation of the activity of a component from the activity of an analogous component in an ideal solution (see Glossary). An ideal solution component would have an activity coefficient equal to one. This characteristic of an ideal solution is utilized in Section 1.3 to derive two different ideal solutions which are in common use.
1.2.3 Phase Equilibrium

Phase equilibrium deals with the thermodynamic conditions necessary if two phases of matter are to coexist at equilibrium. In a simple compressible system containing a single pure component, the conditions for phase equilibrium are that the pressure and temperature must be uniform throughout the system. In such a system, the composition of each phase is the same (pure).

Binary system phase equilibrium is complicated by the fact that each phase will, in general, have a different composition. The thermodynamic variable which accounts for the different composition between phases at equilibrium is the chemical potential. Thus in addition to equality of temperature and pressure, binary system phase equilibrium requires that the value of the chemical potential of each component must be the same in every phase. These conditions can be stated as follows for a binary component system.

\[
\begin{align*}
T_1 &= T_2 \quad (1.62) \\
p_1 &= p_2 \quad (1.63) \\
\mu_1 &= \mu_1 \quad (1.64)
\end{align*}
\]
\[ \mu_2^1 = \mu_2^2 \]  \hspace{1cm} (1.65)

In the above equations, superscripts designate phases and subscripts designate components.

Vapor/liquid equilibrium data consisting of pressure, temperature and composition measurements are frequently useful for inferring the properties of one phase from those of another. For example, if the vapor phase chemical potentials are known by other means, Eqs. 1.64 and 1.65 provide the chemical potentials in the equilibrium liquid phase. This relationship is utilized in the calculation of the thermodynamic properties of LiBr/H_2O found in Chapter 4. The next topic discussed provides an important relationship between chemical potentials in a single phase, the Gibbs-Duhem equation.

1.2.4 Gibbs-Duhem Equation

Consider a solution consisting of \( n_1 \) moles of component 1 and \( n_2 \) moles of component 2. Following from Eq. 1.52, the Gibbs free energy of such a solution obeys

\[ dG = Vdp - SdT + \mu_1dn_1 + \mu_2dn_2 \]  \hspace{1cm} (1.66)

At constant temperature and pressure,

\[ dG = \mu_1dn_1 + \mu_2dn_2 \]  \hspace{1cm} (1.67)
Also, since \( \mu \) represents a partial molal property, it can be concluded from Eq. 1.66 [24] that

\[
G = n_1\mu_1 + n_2\mu_2
\]  

(1.68)

Taking the total differential of the foregoing equation

\[
dG = \mu_1dn_1 + n_1d\mu_1 + \mu_2dn_2 + n_2d\mu_2
\]  

(1.69)

Combining Eqs. 1.67 and 1.69,

\[
n_1d\mu_1 + n_2d\mu_2 = 0
\]  

(1.70)

Equation 1.70 is one of a group of relations known as Gibbs-Duhem equations. A similar relation can be obtained for any partial molal property in place of the chemical potential. The relation presented in Eq. 1.70 is most useful because it is frequently necessary to relate the chemical potential of the components of a solution. For example, when the chemical potential of one component is known, the other one can be calculated using Eq. 1.70.

1.3 Non-electrolyte and Electrolyte Binary Systems

As noted previously, the working fluids used in absorption chillers and heat pumps are binary solutions. Two types of binary solutions are discussed below in separate sections. The first section deals with
non-electrolyte (see Glossary) solutions exemplified by air in liquid or vapor form. The $\text{H}_2\text{O}/\text{NH}_3$ pair also belongs in the non-electrolyte category. The second section deals with electrolyte (see Glossary) solutions. These solutions are exemplified by sea water in which ionic salts (solids) are dissolved in water to form a multi-component liquid solution. The LiBr/$\text{H}_2\text{O}$ pair is a binary electrolyte solution. The examples mentioned are intended to link the subject with common experience. Although non-electrolyte and electrolyte solutions exhibit fundamentally different thermodynamic characteristics, the analysis methods are basically the same. There are, however, several notation and analysis conventions unique to each. These details are emphasized in the developments which follow.

1.3.1 Non-electrolyte Binary Systems

The components of a non-electrolyte solution retain their molecular structure upon mixing. An average molecule of any of the components of such a solution is made up of several (in general) atoms which remain closely bonded indefinitely. One example is the ammonia/water system. The thermodynamic analysis of such solutions consisting of two components is reviewed in this section.
Many measures of composition of a solution are in common use by different investigators. The mole fraction, $X_i$, defined in Eq. 1.54 is used here. This choice is somewhat arbitrary but it is conventional and it leads to a concise analysis.

The chemical potential of either of the components in a binary solution can be represented in the form (presented previously)

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (1.60)$$

The standard state, indicated by superscript $\circ$, must be specified. For the non-electrolyte solutions considered here, the pure component at the temperature and pressure of the solution will be assumed as the standard state of each of the components. Equation 1.60 can be written for component 1 in terms of the mole fraction based activity coefficient $\gamma_i$, as

$$\mu_1 = \mu_1^\circ + RT \ln (X_1 \gamma_1) \quad (1.71)$$

For an ideal solution, the activity coefficient is unity (see Section 1.2.2.2). Therefore, Eq. 1.71 for an ideal solution becomes

$$\mu_1 = \mu_1^\circ + RT \ln X_1 \quad (1.72)$$

The form of the chemical potential of component 2 is
determined from Eq. 1.72 by use of the Gibbs-Duhem equation in the form

\[ d\mu_2 = -\frac{X_1}{X_2} d\mu_1 \]  

(1.73)

With Eq. 1.72, integration of Eq. 1.73 from the standard state of component 2 \((X_2^0 = 1)\) to an arbitrary state results in

\[ \mu_2 = \mu_2^0 + RT \ln X_2 \]  

(1.74)

\[ = \mu_2^0 + RT \ln (1-X_1) \]

where the partial molal Gibbs free energy in the standard state, \(\mu_2^0\), has been introduced following Eq. 1.60. Using Eqs. 1.68, 1.71 and 1.74, the Gibbs free energy for an ideal solution can be written as

\[ G = \frac{G}{n_1 + n_2} \]  

(1.75)

\[ = X_1 \mu_1^0 + (1-X_1)\mu_2^0 + RT[X_1 \ln X_1 + (1-X_1)\ln(1-X_1)] \]

The ideal solution presented here is an excellent model of the mixing of two components that do not interact. An ideal gas mixture is an example [24]. The ideal solution model is an excellent approximation of some "real" solutions involving molecules of the same
size where the intermolecular forces between molecules of the same type are the same as the forces between the different types. Solutions composed of molecules that differ only in isotopic composition [27] provide an example.

Most binary solutions deviate significantly from the ideal solution model. The properties of these "real" solutions can be represented in the general form of Eq. 1.75 by adding a term, \( g_{ex}(T,p,X) \), which accounts for the difference between the molar Gibbs free energy of an actual solution and the value predicted by the ideal model. This term is known as an excess function [27,46]. Thus, the Gibbs free energy is more generally expressed as

\[
g(T,p,X) = X_1 \mu_1^\circ + (1-X_1) \mu_2^\circ +
\]

\[\quad + RT[X_1 \ln X_1 + (1-X_1) \ln(1-X_1)] + \quad \text{(1.76)}\]

\[\quad + g_{ex}(T,p,X_1)\]

The functional dependence on temperature, pressure and concentration of the excess Gibbs free energy in Eq. 1.76 is not well understood for most solutions. By necessity then, application of Eq. 1.76 requires experimental data (for an example see [44]).
1.3.2 Electrolyte Binary Systems

An electrolyte is a solute that dissociates, in solution, into ions. A weak electrolyte dissociates only partially. Strong electrolytes, like LiBr, dissociate almost completely in aqueous solution. Electrolyte solution thermodynamics is basically the same as the development introduced in Section 1.3.1. Some notation and convention differences arise, however, due to the special characteristics of electrolytes.

The electrolyte standard state is chosen (following convention) to be a hypothetical, one molal solution at the temperature and pressure of the system under study. Thus the properties of the standard state are dependent on temperature and pressure. The standard state is further defined by specifying the fugacity of the electrolyte. The fugacity is obtained by extrapolating (linearly) from the solution characteristics at infinite dilution. The limiting relation used for the extrapolation is as follows.

\[
\lim_{m \to 0} \frac{f^0_2}{m} = \lim_{m \to 0} \frac{f_2}{m^2} \quad (1.77)
\]

Where \( m \) is the molality of the solute defined by
The subscript 2 refers to the electrolyte (i.e. LiBr in a LiBr/H₂O solution).

Dissociation of the electrolyte molecules leads to consideration of the individual activities of the ions. This leads further to the definition of a mean activity for the ions. For an electrolyte such as LiBr, the mean activity of the ions, \( a^\pm \), is defined as

\[
\frac{a^\pm}{a_2} = (a_2)^{1/2}
\]  

(1.79)

This leads to an expression for the chemical potential of the LiBr in solution as follows

\[
\mu_2 = \mu_2^o + RT \ln a_2
\]

(1.80)

\[
= \mu_2^o + 2RT \ln a^\pm
\]

Furthermore, it is common to define a mean activity coefficient, \( \gamma^\pm \), for an electrolyte as follows,

\[
\gamma^\pm = \frac{a^\pm}{m}
\]

(1.81)

The chemical potential is then,

\[
\mu_2 = \mu_2^o + 2RT \ln (m \gamma^\pm)
\]

(1.82)
The use of mean activities and mean activity coefficients is very common in electrolyte solution investigations. In fact, the subscript \( i \) denoting the mean value is frequently omitted in the literature and it is left to the reader to understand the context. For clarity, the subscript will be included in the present work.

In general, an activity coefficient represents the deviation from the ideal solution characteristic. The ideal electrolyte solution can be defined by setting \( \gamma_i \) equal to unity in Eq. 1.82. The result is,

\[
\mu_2 = \mu_2^0 + 2RT\ln m \quad (1.83)
\]

At constant temperature and pressure, the differential is then,

\[
d\mu_2 = 2RTd(\ln m) \quad (1.84)
\]

Application of the Gibbs-Duhem equation will yield the appropriate form for the chemical potential of the solvent (for the ideal electrolyte solution). The Gibbs-Duhem equation states that,
\[ d\mu_1 = -\frac{n_2}{n_1}d\mu_2 \]
\[ = -\frac{n_2}{n_1}2RTd(ln m) \]

Note that the molality is related to the molar density of the components as follows,

\[ m = \frac{n_2}{n_1} \]

(1.86)

Where \( n_m \) is the number of moles of solvent per kg of solvent. Thus Eq. 1.85 becomes,

\[ d\mu_1 = \frac{-2RT}{n_m}dm \]

(1.87)

Integration of Eq. 1.87 from the solvent standard state \((m=0)\) to an arbitrary molality, \( m \), yields,

\[ \mu_1 = \mu_1^o - \frac{2RT}{n_m}m \]

(1.88)

where the solvent standard state, \( \mu_1^o \), has been introduced following Eq. 1.60. The Gibbs free energy for an ideal electrolyte solution is then

\[ G = n_1\mu_1^o + n_2\mu_2^o - \frac{n_12RT}{n_m}m + n_2RT\ln m \]

(1.89)
For electrolyte solutions it is common to see the Gibbs free energy expressed per kg of solvent as follows,

\[ G_m = \frac{n_m \mu_1^* + m \mu_2^* - 2RTm + 2RTm \ln(m)}{n_1} \]  

(1.90)

Real electrolyte solution properties deviate from the ideal solution but the two can be related by adding an excess term to Eq. 1.90 [46]. This is analogous to the excess term of Eq. 1.76, but it must be noted carefully that the definition of the ideal solution is not the same in both cases. Thus the Gibbs free energy for an electrolyte solution can be expressed more generally as

\[ \frac{G(T,p,m)}{n_1/n_m} = \frac{n_m \mu_1^* + m \mu_2^* - 2RTm + 2RTm \ln(m)}{n_1/n_m} \]  

(1.91)

A concise expression for the excess Gibbs free energy can be obtained by defining the osmotic coefficient, \( \phi_p \). This quantity is sometimes called the practical osmotic coefficient [27]. The osmotic coefficient of the water in LiBr/H\(_2\)O is defined as
The osmotic coefficient is a measure of the activity of the water. The standard state of water is taken to be the pure liquid at the temperature and pressure of the system under study. Substitution of Eqs. 1.60, 1.82 and 1.92 into Eq. 1.68 results in

\[ G = n_1 [\mu_1^o - \frac{2mRT}{n_1} \phi_p] + n_2 [\mu_2^o + 2RT \ln (m \gamma_2)] \]  

(1.93)

Next, subtract out the ideal solution terms (Eq. 1.89) to give

\[ G_{ex} = \frac{2n_1 mRT}{n_1} (1 - \phi_p) + n_2 2RT \ln \gamma_1 \]  

(1.94)

Or on a per kg of water basis

\[ \frac{G_{ex}}{n_1/n_m} = 2mRT (1 - \phi_p + \ln \gamma_1) \]  

(1.95)

Equation 1.95 contains nothing fundamentally new but it provides a concise expression for the excess Gibbs free energy and it will be used in Chapter 2.

As for the previously considered case of non-electrolyte solutions, the excess Gibbs free energy
for electrolyte solutions is not well understood. However, some theoretical advances have been made which predict \( G_{ex} \) quite well at low electrolyte concentrations (\( m < 0.1 \text{ mol/kg} \)). Specifically, the Debye-Huckel [10] theory of long range electrostatic interactions is well supported by experiment. However, since the concentration range of interest in the current work is approximately \( 0 \to 20 \text{ mol/kg} \), the theory contributes only a limiting law in the low concentration range. Additional theoretical advances can be found in the work of Mayer [32]. This statistical mechanics approach has not been refined to the point where it is useful for numerical evaluation.

The current theories are not adequate for the purpose of predicting thermodynamic properties of electrolyte solutions. Therefore, empirical approaches must be considered. The work of Pitzer [39,40] represents the best example of an empirical approach based on up-to-date theory. The empirical correlation of the properties of the solution LiBr/H\(_2\)O which will be presented in Chapters 2 to 5 is an extension of the work of Pitzer.
1.4 Thermodynamic Property Calculations

One of the major goals of this work is to provide a means by which the thermodynamic properties of LiBr/H₂O can be calculated. Previously published compilations [31,33] of calculated thermodynamic properties of this fluid pair are not complete enough to support the thermodynamic analysis needed to understand absorption cycles fully. The present work provides a direct means to calculate any thermodynamic property of LiBr/H₂O, given a set of values of the independent variables, temperature, pressure and composition.

The thermodynamic property calculation method employed in this work is termed here the free energy surface (FES) method because it involves the generation of a free energy "surface" as a function of the independent variables as a prerequisite to property calculations. In general, this may be a Gibbs free energy function or a Helmholtz free energy function. The FES method is characterized by extensive data analysis performed prior to any property calculations. However, once this preliminary data analysis is complete, the FES method enables reasonably routine property calculations to be conducted. A general description of the FES method is presented next. A detailed account of the
application of the method to the pair LiBr/H\textsubscript{2}O is presented in Chapters 2 to 5. An application of the FES method to H\textsubscript{2}O/NH\textsubscript{3} was published previously by Schulz [44].

The data analysis facet of the FES method consists of obtaining an analytic expression for the free energy of the system of interest. The method of obtaining the analytic expression is based on calculating a least squares estimate of a set of arbitrary parameters which are included in a candidate functional form for the free energy. Property data are introduced into the least squares computation. The resulting analytic expression for the Gibbs free energy is then used to calculate other thermodynamic properties of the system.

The FES method is introduced by describing several previously published examples of its use. These examples include two applications to pure substances (H\textsubscript{2}O and NH\textsubscript{3}) and one application to an absorption pair (H\textsubscript{2}O/NH\textsubscript{3}). In the case of a pure substance, the free energy surface is a function of two independent variables. The functional relationship follows from the state principle for a simple compressible system containing a pure component. The surface is relatively easy to visualize because it exists (or is embedded) in a 3 dimensional variable space. This is not the case
for the free energy surface of a binary component, simple compressible system, however. In this case, the free energy is dependent on three independent variables, and thus is a 3 dimensional "hypersurface" existing (or embedded) in a 4 dimensional variable space. Nevertheless, the mathematical treatment of both cases is fundamentally the same. A description of the free energy surface method applied to a pure component is presented next, followed by a discussion of its application to binary component systems.

Application of the FES method to a pure component requires that a pair of independent thermodynamic variables be chosen first. A dependent thermodynamic variable possessing a unique characteristic is then sought. The unique characteristic is that any thermodynamic property must be expressible in terms of the dependent variable and its derivatives with respect to the independent variables. For example, if the independent variables are chosen to be temperature and pressure, then the Gibbs free energy is found to possess the characteristic. Alternatively, the choice of temperature and density as the independent variables leads to the Helmholtz free energy as the dependent variable possessing the characteristic.

The fact that the free energy functions possess the
desired characteristic is presented here without formal proof. However, the characteristic can be simply demonstrated for particular thermodynamic properties. Consider the case where temperature and pressure are independent. The following equations express the volume, entropy, enthalpy and specific heat in terms of the Gibbs free energy and its derivatives with respect to temperature and pressure.

\[ v = \frac{\partial g}{\partial p} \text{ } \text{(1.96)} \]

\[ s = -\frac{\partial g}{\partial T} \text{ } \text{p} \text{ } \text{(1.97)} \]

\[ h = g - T\left(-\frac{\partial g}{\partial T}\right) \text{ } \text{p} \text{ } \text{(1.98)} \]

\[ c_p = -T\left(-\frac{\partial^2 g}{\partial T^2}\right) \text{ } \text{p} \text{ } \text{(1.99)} \]

Note that Eqs. 1.96 and 1.97 follow directly from Eqs. 1.26 and 1.27. Equation 1.98 follows from Eq. 1.97 and the definition of the Gibbs free energy (Eq. 1.8). Equation 1.99 follows from Eq. 1.98 and the definition of the specific heat (Eq. 1.33). Equations 1.96 to 1.99 are a representative sample of the simple thermodynamic
property expressions which can be derived when the Gibbs free energy is known as a function of the temperature and pressure.

As a result of the fact that the thermodynamic properties can be expressed in terms of the Gibbs free energy and its derivatives with respect to temperature and pressure, the FES method can employ several types of experimental data simultaneously in the generation of the free energy surface. For example, if volumetric and specific heat data are available for a pure substance as a function of temperature and pressure, then the FES method would proceed as follows. First, a functional form for the Gibbs free energy would be chosen. The functional form expresses the Gibbs free energy in terms of the temperature, pressure and a set of undetermined coefficients. Next, expressions for the volume and the specific heat would be derived in terms of the undetermined coefficients using Eqs. 1.96 and 1.99. Finally, the coefficients would be determined by minimizing the squared error between the experimental data and the analytic expressions for the volume and the specific heat. The entropy and the enthalpy could then be calculated using Eqs. 1.97 and 1.98.

An analogous method, based on the Helmholtz free energy, is applicable when the independent variables are
temperature and density. This choice of independent variables has the advantage (over temperature and pressure) of being independent for every possible state of the system, including the saturation states. The disadvantage is that temperature and pressure are more commonly measured in the laboratory and use of the Helmholtz free energy surface requires iteration to find the density which matches a given temperature and pressure. Helmholtz free energy surfaces have been determined using experimental data for water [23] and ammonia [16]. The surface for water requires 58 constants while the surface for ammonia requires 55 constants. The property predictions from these analytic surfaces are remarkably accurate over a wide range of conditions. In fact, for both substances the property data derived from the analytic surface represents the experimental data with sufficient accuracy so that the derived properties have been accepted as the best available data. In the present work, property values for water are generated, as needed, from the analytic surface reported in [23].

The FES method described above can be extended to simple compressible binary component systems such as LiBr/H$_2$O and H$_2$O/NH$_3$. Due to the additional component, three independent variables must be specified to fix the
state of such a system. The choice of temperature, pressure and composition leads to the Gibbs free energy as the property from which any other thermodynamic property can be derived most directly. A recent application of the FES method to H₂O/NH₃ involves 36 constants [44]. The results are accurate enough for some absorption system design calculations and no further discussion of this absorption pair is provided in the present study. Details of the application of the FES method to LiBr/H₂O can be found in Chapters 2 to 5.

The quality of the thermodynamic data generated using the FES method depends on several factors. For example, the quality and quantity of the experimental data are important. Also, the functional dependence of the free energy (chosen by the analyst) on the independent variables is important. The ability of the method to reproduce the experimental data used to generate the surface is a fundamental test. The ability of the method to extrapolate accurately beyond the range of the experimental data is expected to be limited. All of these points will be addressed in the discussion of the accuracy of the property predictions in Chapter 5.

The free energy surface method provides a powerful means of access to thermodynamic data about a particular system. However, generation of the analytic surface
requires substantial data analysis and is computationally intense. The details of the application of the method to LiBr/H$_2$O are presented next.
Chapter 2

LiBr/H₂O Gibbs Free Energy

This chapter is mainly concerned with discussing the functional dependence of the Gibbs free energy of LiBr/H₂O on the independent variables temperature, pressure and composition. As discussed here, the functional dependence includes a combination of theoretical terms and higher order empirical terms. The higher order terms are required in order to extend the applicability of the functional form beyond the range of accuracy possible using the theoretical terms only. The functional form obtained is used later in this study to represent empirical property data for LiBr/H₂O by imposing the least squares criterion. This type of approach is sometimes referred to as a semi-empirical approach.
2.1 Debye-Huckel Theory

A publication by Debye and Huckel [10] in 1923 was a key step in the evolution of understanding of electrolyte solutions. The Debye-Huckel theory which accounts for the electrostatic forces between ions in solution explained a large body of apparently anomalous experimental data. In the intervening decades many investigators have proposed improvements; however, the principal assumptions of the theory remain valid. These assumptions will be introduced next. A complete review of the Debye-Huckel theory can be found elsewhere [19,41].

Dissociation of the electrolyte molecules into ions occurs when an electrolyte such as LiBr is dissolved in H₂O. A central assumption of the Debye-Huckel theory is that the dissociation is complete. This means that all of the electrolyte ions are free to move about individually in the solution. This assumption enabled Debye and Huckel to calculate the charge density and electric field strength surrounding a particular ion.

The ions are assumed to be all of the same size and suspended in a dielectric medium exhibiting the dielectric constant of the pure solvent. These basic assumptions allow formulation of a differential equation.
(a Poisson equation) representing the electric field strength variations in space around a single ion. A closed form solution of the equation for the electric field strength is made possible by linearization. The resulting expression for the electric field strength allowed Debye and Huckel to calculate the contribution to the Gibbs free energy from electrostatic forces. The theory is very successful at modeling observed phenomena for low concentrations of electrolytes (less than 0.1 mol/kg).

2.2 Pitzer Modification of the Debye-Huckel Theory

The composition range of accuracy of the original Debye-Huckel formulation has been extended by various improvements to the theory. An alternate derivation (with the same principal assumptions) by Pitzer [39] has been shown to have good accuracy to approximately 0.5 mol/kg. Note that the composition range of interest in absorption system analysis is approximately 0-20 mol/kg. Pitzer's modification of the Debye-Huckel result for LiBr/H₂O can be written as
ln \( \gamma_\pm \) = \( f_{\text{PDH}}(m) \)
\[
= -A_{\text{DH}} \left( \frac{m^{1/2}}{1 + B m^{1/2}} \right) + \frac{2}{B} \ln(1 + B m^{1/2})
\]

where,
\[
A_{\text{DH}} = \frac{(e^0)^3 (2\pi N a m^0)^{1/2}}{(4\pi \varepsilon_0 k_\text{B} \varepsilon_\text{A} T)^{3/2}}
\]

The symbols denote:

- \( \gamma_\pm \) - mean activity coefficient of LiBr
- \( m \) - dimensionless molality
- \( A_{\text{DH}} \) - Debye-Huckel constant (dimensionless)
- \( B \) - Constant = 1.2 (dimensionless)
- \( \rho \) - density of water
- \( N_a \) - Avogadro's number
- \( e^0 \) - fundamental electric charge
- \( \varepsilon_0 \) - permittivity of free space
- \( k_\text{B} \) - Boltzmann constant
- \( \varepsilon_\text{A} \) - dielectric constant of water
- \( m^0 \) - conventional molality of the standard state of LiBr = 1 mol/kg
- \( \pi \) - fundamental constant (3.14159...)
The dimensionless molality, \( m \), is defined as

\[
m = \frac{m^*}{m^0}
\]  

(2.3)

where

\( m^* \) - conventional molality (mol/kg)

\( m^0 \) - conventional molality of the standard state of LiBr = 1.0 mol/kg.

Use of the dimensionless molality, \( m \), leads to dimensionless forms for the empirical constants which arise later in the analysis. Since the divisor in Eq. 2.3 is unity, the dimensionless molality is numerically equal to the conventional molality in mol/kg.

2.3 Pitzer Semi-Empirical Approach

In Reference [39] Pitzer utilized his modification of the Debye-Huckel theory as the leading term in an expression for the mean activity coefficient of electrolytes in solution. This expression includes several higher order empirical terms which extend the applicability of the expression to higher concentrations. Pitzer's expression for LiBr in aqueous solution is presented in this section. It is noteworthy that
Pitzer's expression accounts only for the composition dependence of the mean activity coefficient. Utilization of this expression requires that the temperature and pressure be constant. This restriction is removed in Section 2.4, to follow, where Pitzer's approach is extended.

Pitzer's theoretical analysis provides some information about the composition dependence of the higher order terms. According to Pitzer, the mean activity coefficient of LiBr can be written as

\[ \ln \gamma_+ = f_{PDH}(m) + f_{CD}(m)m + Em^2 \] (2.4)

where,

\[ f_{CD}(m) = 2C + \frac{2D}{\alpha m} \left\{ 1 - (1 + \alpha m^{1/2} - - -) \exp(-\alpha m^{1/2}) \right\} \] (2.5)

The symbols denote:

- \( f_{PDH}(m) \) - Pitzer Debye-Huckel term defined in Eq. 2.1
- \( \alpha \) - Constant = 2.0 (dimensionless)
- \( C,D,E \) - arbitrary constants which are adjusted to fit the data (dimensionless)

Based on the semi-empirical approach represented by Eq. 2.4, Pitzer has presented [40] an extensive tabulation of thermodynamic correlations for a wide
range of aqueous electrolyte systems at constant temperature and pressure.

The expression for the mean activity coefficient of LiBr in Eq. 2.4 can be used to obtain an expression for the excess Gibbs free energy of the solution. The first step is to obtain an expression for the osmotic coefficient of the water. Rearranging the Gibbs-Duhem equation (Eq. 1.70) in terms of the activity results in

\[ \frac{d(ln a_1)}{n_1 RT} = \frac{-n_2 du_2}{n_1 RT} \]  \hspace{1cm} (2.6)

Integrating at constant temperature and pressure, from \( m=0 \) to an arbitrary molality \( m \), with Eqs. 1.82 and 2.4 gives

\[ \ln a_1 = \int_{0}^{m} \frac{-n_2 du_2}{n_1 RT} \]

\[ = \frac{m^{3/2}}{1 + \lambda m^{1/2} - 2\lambda Cm^2 + \frac{4}{\lambda E m^3}} \]  \hspace{1cm} (2.7)

where

\[ \lambda = m^0 M_1 \]  \hspace{1cm} (2.8)

in which \( M_1 \) is the molecular weight of \( H_2O \). Using
Eq. 2.7 and the definition of the osmotic coefficient in Eq. 1.92, the expression for the osmotic coefficient becomes

\[
1 - \phi_p = \frac{A_{DHm}^{1/2}}{1 + Bm^{1/2}} - Cm + \frac{(Dm)\exp(-\alpha m^{1/2})}{3} - \frac{Em^2}{3}
\]

(2.9)

Next, define a dimensionless temperature, \( \theta \), as

\[
\theta = \frac{T}{T_s}
\]

(2.10)

where \( T_s \) is a reference temperature taken as 100.0 K.

The dimensionless excess Gibbs free energy per kg of H\(_2\)O is obtained by substituting Eqs. 2.4 and 2.9 into Eq. 1.95 and by using Eq. 2.10.

\[
\frac{G_{ex}}{n_1 \lambda RT_s} = \frac{-4\theta \lambda m}{B} \ln(1 + Bm^{1/2}) + 2\theta Cm^2 + \frac{4\theta Dm}{\alpha} - \frac{1 - (1 + \alpha m^{1/2})\exp(-\alpha m^{1/2})}{3} + \frac{2\theta E}{3}
\]

(2.11)
where,

\[ n_1 \quad \text{number of moles of } H_2O \]

\[ R \quad \text{gas constant} \]

Equation 2.11 is a dimensionless form of Pitzer's result. Thermodynamic data for a wide range of electrolytes [40] at a single temperature and pressure can be successfully correlated using Eq. 2.11 with C, D and E as constants.

2.4 Extensions of the Pitzer Semi-empirical Approach

Developed in the Current Study

Motivation for the extension of the Pitzer semi-empirical approach stems from the need to represent thermodynamic data over a range of temperatures and pressures. The extension is accomplished in the current study by allowing C, D and E in Eq. 2.11 to be functions of temperature and pressure. This is emphasized in the following expression for the dimensionless Gibbs free energy which indicates the dependence on temperature, pressure and composition of the various terms.
Equation 2.12 is a key result in the current study. It will be referred to frequently in subsequent discussions. The object of this section, however, is to discuss the temperature and pressure dependence of C, D and E.

The theoretical studies of liquid solutions found in the literature have not offered any guide as to the appropriate functional form for the temperature and pressure dependence of the Gibbs free energy. In the current study an empirical approach to the problem of specifying a functional form for C, D and E is used. Three candidate functional forms for the pressure and temperature dependence of C, D and E in Eq. 2.12 were selected for testing based on related work. The ability of these forms to reproduce the pressure and temperature dependence of the experimental data is the measure of
their usefulness. Details of the results obtained from the least squares procedure, including the best choice of the three functional forms, are presented in Chapter 5.

Three separate least squares computations were performed to obtain a best choice among the three formulations. Within each formulation, identical functional forms were used for the pressure and temperature dependence of $C$, $D$ and $E$. Note that in each case, the functional forms selected involve the constants linearly. This linearity provides computational benefits in the evaluation of the constants as discussed in Chapter 3. The first formulation defines $C$, $D$ and $E$ as follows.

\[
C(\theta, \pi) = \frac{C_1 + C_2 \pi + C_3 \pi^2}{\theta} + \frac{C_4 + C_5 \pi + C_6 \pi^2}{\theta^2} + \frac{C_7 + C_8 \pi + C_9 \pi^2}{\theta^3} \tag{2.13}
\]

\[
D(\theta, \pi) = \frac{D_1 + D_2 \pi + D_3 \pi^2}{\theta} + \frac{D_4 + D_5 \pi + D_6 \pi^2}{\theta^2} + \frac{D_7 + D_8 \pi + D_9 \pi^2}{\theta^3} \tag{2.14}
\]

\[
E(\theta, \pi) = \frac{E_1 + E_2 \pi + E_3 \pi^2}{\theta} + \frac{E_4 + E_5 \pi + E_6 \pi^2}{\theta^2} + \frac{E_7 + E_8 \pi + E_9 \pi^2}{\theta^3} \tag{2.15}
\]

Where $\pi$ is a dimensionless pressure defined as
\[ P = \frac{\pi}{\pi_s} \]  
(2.16)

and \( \pi_s \) is a reference pressure taken to be 10.0 bar. Although the functional forms of \( C, D \) and \( E \) are identical in Eqs. 2.13 to 2.15, the undetermined constants which appear (\( C_i, D_i \) and \( E_i \), \( i=1,2,\ldots,9 \)) define \( C, D \) and \( E \) uniquely.

The second and third formulations define \( C, D \) and \( E \) according to the following functional forms. Note that for brevity, only the expression for \( C \) is given in each case.

\[
C(\theta,\pi) = C_1 + C_2 + C_3 \theta + C_4 \theta^2 + C_5 \pi \theta + C_6 \pi + \\
+ C_7 \pi^2 + C_8 \frac{\pi}{\theta} + C_9 \frac{\pi^2}{\theta^2} + C_{10} \frac{\pi^3}{\theta^3} \tag{2.17}
\]

\[
C(\theta,\pi) = C_1 + \frac{C_2}{\theta} + \frac{C_3}{\theta^2} + \frac{C_4}{\theta^3} + C_5 \frac{\pi}{\theta^2} + C_6 \frac{\pi}{\theta} \tag{2.18}
+ C_7 \frac{\pi^2}{\theta} + C_8 \pi + C_9 \pi^2 + C_{10} \pi^3
\]

A brief discussion of the origin of the three candidate functional forms is presented next. Equations 2.13 to 2.15 can be traced to Schulz [44]. In
[44], a similar functional form is used to represent the temperature and pressure dependence of the Gibbs free energy of $H_2O/NH_3$. Although Schulz gives no compelling justification for the use of this functional form, its success in representing the properties of the binary solution $H_2O/NH_3$ suggested its use in the present study.

The two other functional forms (Eqs. 2.17 and 2.18) are motivated by considerations discussed in detail by Fortier and Desnoyers [14]. These functional forms result from a series of choices. Details of the reasoning behind these choices are included as Appendix B. The final section of this chapter, which follows immediately, deals with the temperature and pressure dependence of the second term in Eq. 2.12, $X_2\mu_2^\circ(\theta,\tau)/(RT)$. This term accounts for the contribution of the standard state chemical potential of LiBr, $\mu_2^\circ$.

2.5 LiBr Standard State Representation

For the purpose of generating an analytic Gibbs free energy surface for LiBr/$H_2O$, an expression for the partial molal Gibbs free energy of LiBr in its standard state, $\mu_2^\circ(T,p)$, is required. This quantity is defined in Section 1.3.2 for an electrolyte such as LiBr. The
standard state has a fixed composition (1.0 mol/kg) and has the temperature and pressure of the system under study. Thus the standard state properties are functions of temperature and pressure.

Very little data on the properties of the standard state of LiBr are available. Only one source has been found. In this source, Eigen and Wicke [111] have estimated the partial molal specific heat at the standard state from experimental data. However, for the present purpose, insufficient data is available to define clearly the standard state properties. The alternative is to infer the standard state properties from data on solution properties. The inference is made by representing the standard state chemical potential of LiBr as a function of temperature and pressure which involves a set of undetermined constants. Values for these constants are determined later in a least squares computation. The functional form chosen for the dependence of the standard state Gibbs free energy of LiBr on temperature and pressure is discussed next.

Following Schulz [44], the functional form used for the standard state partial molal Gibbs free energy will now be derived from assumed forms for the partial molal volume, $v_2^\circ$, and the partial molal specific heat, $c_{p2}^\circ$, in the standard state. The assumed forms are
\[ v_2^0 = k_1 + k_2p + k_3T + k_4T^2 \]  
\[ c_{p2}^0 = l_1 + l_2T + l_3T^2 \]

The partial molal Gibbs free energy, \( \mu_2^0 \), obeys

\[ d\mu_2^0 = v_2^0 dp - s_2^0dT \]  
\[ (2.21) \]

Where \( s_2^0 \) is the partial molal entropy in the standard state. Integration of Eq. 2.21 from a reference state \((T_0, P_0)\) to an arbitrary state \((T, P)\) yields

\[ \mu_2^0(T, P) = \mu_2^0(T_0, P_0) + \int_{T_0}^{T} v_2^0 dp - \int_{T_0}^{T} s_2^0dT \]

\[ (2.22) \]

where the integration path is illustrated in Figure 1. Note that the definition of the Gibbs free energy (Eq. 1.38) has been invoked.

An expression for \( s_2^0 \) in Eq. 2.22 can be obtained from the following fundamental relation for a simple compressible system of fixed composition (see Eq. 1.30)

\[ ds_2^0 = -\left(\frac{\partial v_2^0}{\partial T}\right)_P dp + \frac{c_{p2}^0}{T}dT \]

\[ (2.23) \]

At constant pressure \((p = P_0)\) the entropy can be written as
Figure 1: Integration Path in Equation 2.22

Figure 2: Integration Path in Equation 2.24
\[ s_{20}^\circ(T_1, P_0) = s_{20}^\circ + \int_{T_0}^{T_1} \frac{c_{p2}^\circ(T, P_0)}{T} \, dT \quad (2.24) \]

The integration path is illustrated in Figure 2. Equation 2.24 can be substituted into the temperature integral in Eq. 2.22 to yield

\[ \int_{T_0}^{T_1} P_1 s_{20}^\circ dT = \int_{T_0}^{T_1} [s_{20}^\circ + \int_{T_0}^{T} -\frac{c_{p2}^\circ}{T} \, dT] \, d\tau \]

\[ = s_{20}^\circ(T_1 - T_0) + \int_{T_0}^{T_1} \frac{c_{p2}^\circ}{T} \, dT \, d\tau \quad (2.25) \]

Substitution of Eq. 2.20 yields

\[ \int_{T_0}^{T_1} P_1 s_{20}^\circ dT = s_{20}^\circ(T_1 - T_0) + l_1 \left[ T_1 \ln \frac{T_1}{T_0} - T_1 + T_0 \right] + \]

\[ + l_2 \left[ -\frac{T_1^2}{2} - T_0^2 \right] - T_0 (T_1 - T_0) \right] + \]

\[ + l_3 \left[ -\frac{T_1^3}{6} - \frac{T_0^3}{2} - \frac{T_0^2}{2} (T_1 - T_0) \right] \quad (2.26) \]

The pressure integral in Eq. 2.22 can be evaluated using Eq. 2.19 to yield

\[ \int_{T_1}^{T_1} P_1 v_{20}^\circ dp = k_1 (p_1 - p_0) + \frac{k_2}{2} (p_1^2 - p_0^2) + \]

\[ + k_3 T_1 (p_1 - p_0) + k_4 T_1^2 (p_1 - p_0) \quad (2.27) \]
Finally, Eq. 2.22 can be written in terms of the results in Eqs. 2.26 and 2.27 as

\[ \mu_2^\circ(T_1, p_1) = h_{20}^\circ - T_1 s_{20}^\circ + l_1 (T_1 - T_0 - T_1 \ln(T_1/T_0)) + \]
\[ + l_2 (T_0 (T_1 - T_0) - (T_1^2 - T_0^2)/2) + \]
\[ + l_3 (T_0^2 (T_1 - T_0)/2 - (T_1^3 - T_0^3)/6) + \]
\[ + k_1 (p_1 - p_0) + k_2 (p_1^2 - p_0^2)/2 + \]
\[ + k_3 T_1 (p_1 - p_0) + k_4 T_1^2 (p_1 - p_0) \]
\]

A dimensionless form of Eq. 2.28 using the dimensionless temperature and pressure (defined in Eqs. 2.10 and 2.16 respectively) can be written as

\[ \frac{\mu_2^\circ(T_1, p_1)}{R T_s} = \frac{h_{20}^\circ}{R T_s} - \frac{s_{20}^\circ}{R T_s} + l_1 \frac{\theta_1 - \theta_0 - \theta_1 \ln(-\theta_1/\theta_0)}{\theta_0} + \]
\[ + l_2 \frac{\theta_0 (\theta_1 - \theta_0) - (\theta_1^2 - \theta_0^2)/2}{\theta_0} + \]
\[ + l_3 \frac{\theta_0^2 (\theta_1 - \theta_0)/2 - (\theta_1^3 - \theta_0^3)/6}{\theta_0} + \]
\[ + k_1 (\pi_1 - \pi_0) + k_2 (\pi_1^2 - \pi_0^2)/2 + \]
\[ + k_3 \theta_1 (\pi_1 - \pi_0) + k_4 \theta_1^2 (\pi_1 - \pi_0) \]
\]

The expression for the standard state partial molal Gibbs free energy presented in Eq. 2.29 involves a reference state denoted by subscript 0. The choice of
the reference state is arbitrary because of the relative nature of properties such as the Gibbs free energy. In thermodynamic calculations, only differences between the Gibbs free energy in two states are of interest and thus the reference state cancels when the same reference state is used throughout. Following [44], the values of pressure and temperature which define the reference state used in this work are \( T_0 = 100 \text{ K} \), \( p_0 = 10 \text{ bar} \).

Two partial molal standard state properties at the reference state temperature and pressure must be specified to evaluate Eq. 2.29. These are the enthalpy, \( h_{20^\circ} \), and the entropy, \( s_{20^\circ} \). Since the thermodynamic calculations considered in this study involve only differences between enthalpy and entropy values in two states, the choice of reference state values is arbitrary. Numerical values for the enthalpy and entropy in the reference state are introduced in Appendix A. Additional discussion of the choice of numerical values is provided in Section 5.5.1.

The seven constants \( (L_1, L_2, L_3, K_1, K_2, K_3, K_4) \) which appear in Eq. 2.29 must be evaluated from experimental data for the solution. The evaluation is accomplished simultaneously with the determination of the constants which define the excess Gibbs free energy by means of a least squares procedure discussed next in Chapter 3.
Chapter 3

Least Squares Formulation

The least squares (LS) method is used in this work to determine the set of constants which define the Gibbs free energy of LiBr/H_2O based on the functional model presented as Eq. 2.12. Details of the LS formulation are presented in Sections 3.1 and 3.2. Section 3.1 introduces a simplified version of the least squares method which cannot be implemented in the present study due to a lack of adequate data. In Section 3.2 another formulation of the least squares method is presented which is used. Finally in Section 3.3 several statistical data measures are discussed that are used in Chapter 5 to evaluate the accuracy of the Gibbs free energy surface. A brief overview of the LS method follows.

The LS method addresses problems described as follows. Given a data set consisting of a single dependent variable and one or more independent variables and given a functional model representing the dependent variable in terms of the independent variables and a set
of undetermined constants, determine the "best" choice of values for the constants. The LS method defines the best choice of constants as the set that minimizes the sum of the squared residual error between the data and the model predictions. The sum is taken over all available data points.

The LS method can be derived [2] from statistical considerations based on the principle of maximum likelihood. According to this principle, values for the constants obtained by the LS method can be interpreted as the most probable estimates, obtainable from a given data set, of the true values of the constants. The true values of the constants are those values which would be obtained by applying the LS method to a hypothetical data set consisting of an infinite number of data points distributed uniformly throughout the range of interest of the independent variables.

In general, the constants may appear in the least squares functional model in any form, including linear and nonlinear forms. This distinction is significant because problems involving only constants which enter linearly can be solved (i.e. the sum of the squared residuals can be minimized yielding values for the constants) by standard linear equation methods which provide an explicit solution. By contrast, the solution
of LS problems in which some of the constants enter nonlinearly requires an iterative search of the multi-dimensional constant space. In the present work, a linear formulation is used to simplify evaluation of the constants.

3.1 A Simplified Least Square Formulation

The free energy surface method (introduced in Section 1.4) of calculating the thermodynamic properties of a system requires an expression for the free energy in terms of the chosen independent variables. The choice made here of temperature, pressure and composition as independent variables for the binary system LiBr/H₂O dictates the use of the Gibbs free energy as the most convenient choice. The proposed functional model of the Gibbs free energy, presented as Eq. 2.12, involves a set of undetermined constants. A simplified form of the methodology for obtaining values of the constants is introduced in this section.

Equation 2.12 can be written in a more compact notation as follows.

\[ g_R = f(\theta, \pi, m ; y_1, \ldots, y_k) \]  

In Eq. 3.1, the independent variables \( \theta, \pi \) and \( m \) appear before the semicolon and the undetermined constants, \( y_i \),
appear following the semi-colon. This notation acknowledges the distinct roles of these two types of quantities. The exact form of $f_g$ and the number of undetermined constants, $k$, depend on which of the three functional forms defined in Eqs. 2.13 to 2.18 are in use. However, the generalized notation in Eq. 3.1 is convenient for introducing the least squares formulation.

The problem, then, is to obtain the best set of values for the constants $y_i$. The least squares method defines the best set as the set that minimizes the weighted sum of the squares of the residuals, $\phi$, defined as follows.

$$\phi = \sum_{i=1}^{N} \frac{1}{\sigma_i^2} (g_{R_i} - f_g(\theta_i, \pi_i, m_i; y_1, \ldots, y_k))^2$$

(3.2)

The terms in Eq. 3.2 are described next individually.

The term $g_{R_i}$ represents dimensionless Gibbs free energy data corresponding to a given set of the independent variables $(\theta_i, \pi_i, m_i)$. The number of data points considered is denoted $N$. The function $f_g$ represents an analytic expression for the dimensionless Gibbs free energy. The differences $(g_{R_i} - f_g)$ are known as the residual errors. The term $\sigma_i$ represents the standard deviation of the dimensionless Gibbs free
energy of a particular data point. In general, a separate standard deviation is associated with each data point in a data set. The standard deviation refers to the distribution of results which would be obtained if the same measurement were repeated many times. The reciprocal of the standard deviation squared, which can be viewed as a weighting factor in the sum, ensures that the data of high accuracy (i.e. low standard deviation) contributes more to the sum than the data of low accuracy.

An explicit solution for the set of constants is made possible by the use of a function which is linear in the undetermined constants. Standard calculus minimization criteria, applied to the quantity $\phi$ in Eq. 3.2, leads to a set of $k$ simultaneous, linear equations in the $k$ constants [2]. Values for the constants, which minimize $\phi$, can be obtained by any standard linear equation solution technique.

For the present investigation, the formulation just presented suffers from a major shortcoming that prevents its utilization: No Gibbs free energy data on LiBr/H$_2$O are available. However, the least squares method just presented forms the basis of the multiproperty formulation which is introduced in the following section. The multiproperty formulation provides a link between available data and the constants $y_i$. 
3.2 Multiproperty Least Square Formulation

The previous section presented a simplified formulation, the implementation of which was not possible in the present study because of a lack of Gibbs free energy data for LiBr/H₂O. In this section another formulation of the same problem is presented which is based on four properties for which data on LiBr/H₂O are available. These four properties are the isobaric specific heat, the density, the chemical potential of H₂O, and the mean activity coefficient of LiBr. Note that similar formulations based on other properties are also possible. The choice of these four properties was based on data availability. For a detailed discussion of the data set used, see Chapter 4.

Multiproperty approaches, similar to the formulation presented in this section, have been reported previously [9,23,29,44]. Also, theoretical support for the method has appeared in the literature [20]. A multiproperty approach forms a synthesis of the thermodynamic information available in the various data sets. The result, in this work, is an expression for the Gibbs free energy of LiBr/H₂O representing the best available thermodynamic data. Details of the multiproperty formulation follow.
The relationships between the properties of interest (i.e., those for which data are available) and the Gibbs free energy are the fundamental links which allow information about the Gibbs free energy to be extracted from the available data. These relationships, which follow directly from the definitions in Chapter 1, are written next in dimensionless form.

\[ \frac{c_pR}{R} = -\theta \left( \frac{\partial g}{\partial \theta} \right)_{T,m} \]  

\[ \frac{1}{\rho_R} = \frac{\rho}{\rho_R} = \frac{\partial g}{\partial \pi} \]  

\[ \frac{\mu_{RL}}{RT} = \frac{\sigma_R}{RT} + n \left( \frac{\partial g}{\partial n} \right)_{T,m} \]  

\[ \ln \gamma_1 = \frac{1}{2\theta} \frac{\partial g}{\partial n_2} - \frac{\mu^e}{2RT \theta} - \ln(m) \]

Note that the expression for the density is presented in inverted form because this form leads to a linear least squares formulation. Also, the expression for the activity coefficient is presented in logarithmic form for notational simplicity.

The least squares formulation is facilitated by introducing the following functional notation similar to that used in Eq. 3.1.
The four functions introduced in Eqs. 3.7 to 3.10 are related to the function $f_\theta$ defined in Eq. 3.1 by the relationships in Eqs. 3.3 to 3.6. It should be noted here that in each of Eqs. 3.7 to 3.10 several of the constants $y_j$ are eliminated when the expressions are expanded. The expanded forms of Eqs. 3.7 to 3.10 appear in Appendix A. Thus each property only contributes information about a subset of the constants which define the Gibbs free energy. However, when combined into the multiproperty formulation, the union of these subsets is the full set of undetermined constants.

The multiproperty least squares criterion for the best set of constants is identical to the standard least squares criterion: minimization of the weighted sum of the squares of the residuals. The weighted squared residuals of all four types of property data are added together to form $\phi$. The contribution of each data point is normalized by a weighting factor. The weighting
factor is equal to the reciprocal of the standard deviation (of that data point) squared. Thus the weighted squared residuals are dimensionless quantities. The minimization of $\phi$ to obtain the best set of the constants $y_i$ is the final step.

The weighted sum of the squared residuals, denoted $\phi$, can be written as follows.

$$
\phi = \sum_{i=1}^{1} \frac{1}{\sigma_{ci}^2} \left( c_{pi} - f_c(\theta_i, \pi_i, m_i ; y_1, \ldots, y_k) \right)^2 + \\
+ \sum_{i=1}^{q} \frac{1}{\sigma_{vi}^2} \left( v_i - f_v(\theta_i, \pi_i, m_i ; y_1, \ldots, y_k) \right)^2 + \\
+ \sum_{i=1}^{t} \frac{1}{\sigma_{mi}^2} \left( m_i - f_m(\theta_i, \pi_i, m_i ; y_1, \ldots, y_k) \right)^2 + \\
+ \sum_{i=1}^{u} \frac{1}{\sigma_{gi}^2} \left( g_i - f_g(\theta_i, \pi_i, m_i ; y_1, \ldots, y_k) \right)^2
$$

By examination of Eq. 3.11, this formulation can be seen to be an extension of the formulation presented in the previous section. The minimization methods discussed earlier are again applicable here. Care was taken to consider only functional forms which involve the constants $y_i$ linearly. Note that the choice of properties to include can also affect the linearity of the least squares formulation. This is why the density data is included in reciprocal form. The function $\phi$ in
Eq. 3.11 can be minimized to obtain the best set of constants by solving a set of \( k \) simultaneous linear equations. The resulting set of constants defines the Gibbs free energy of LiBr/H\(_2\)O through Eq. 3.1.

After the LS computations are completed, the quality of the model of LiBr/H\(_2\)O can be inferred from its ability to reproduce the input data. Because of the large number of data points included in the computation, the agreement is best measured by statistical variables. The next section defines several statistical variables which are utilized in Chapter 5 to characterize the Gibbs free energy surface model of LiBr/H\(_2\)O.

3.3 Statistical Measures

A measure of the quality of the results obtained from the least squares computation is the ability of the Gibbs free energy surface to reproduce the input data. Because more than 800 data points are involved in the computation for LiBr/H\(_2\)O, the comparison of individual data points is an daunting task. Therefore, a statistical approach is taken in this study. Several measures are introduced next which represent the quality of the Gibbs free energy surface model in a statistical sense. The statistical measures were computed for each of the four types of input data. Results of these computations are presented in Chapter 5.
The statistical measures are presented in terms of a generic thermodynamic property, $\Omega$, as follows.

$$\Omega = f_\omega(\theta, \pi, m; y_1, \ldots, y_k)$$ (3.12)

Equation 3.12 is a generalized form of Eqs. 3.1 and 3.7 to 3.10. The weighting factor, $w_\omega$, for each data point is

$$w_{\omega i} = \frac{1}{\sigma_{\omega i}}$$ (3.13)

where $\sigma_{\omega i}$ is the standard deviation of data point $i$.

The weighted mean error $\varepsilon_\pm$ is defined as

$$\varepsilon_\pm = \frac{N}{\sum_{i=1}^{N} w_{\omega i} [\Omega_i - f_\omega(\theta, \pi, m; y_1, \ldots, y_k)\}}$$ (3.14)

The weighted root mean square (RMS) error $\varepsilon_{\text{RMS}}$ is defined as

$$[\varepsilon_{\text{RMS}}]^2 = \frac{N}{\sum_{i=1}^{N} w_{\omega i}} \left\{ \sum_{i=1}^{N} w_{\omega i} [\Omega_i - f_\omega(\theta, \pi, m_i; y_1, \ldots, y_k)]^2 \right\}$$ (3.15)

The mean error and the RMS error defined above are
fundamental statistics representing the problem of interest. In statistical terminology, they represent respectively the first moment about the origin and the second moment about the mean.

Another statistical measure which is particularly suited to the least squares problem is the squared multiple correlation coefficient $R^2$ [2]. This quantity is defined as

$$R^2 = 1 - \frac{\sum_{i=1}^{N} w_i \left[ \Omega_i - f(\theta, \pi_i, m_i ; y_1, \ldots, y_k) \right]^2}{\sum_{i=1}^{N} w_i}$$  \hspace{1cm} (3.16)$$

where

$$\Omega_i = \frac{\sum_{i=1}^{N} w_i \Omega_i}{\sum_{i=1}^{N} w_i}$$  \hspace{1cm} (3.17)$$

The fraction in Eq. 3.16 represents a ratio between the variability of the residual error and the variability of the data set. Thus, the multiple correlation coefficient represents the fraction of the total variation in the data set accounted for by the fitted equation. When $R^2$ is close to unity, a high quality fit is implied.
The three statistical measures defined in Eqs. 3.14 to 3.16 are used in Chapter 5 to help quantify the quality of fit of the Gibbs free energy surface for LiBr/H$_2$O. Before proceeding to a consideration of the results, a discussion of the data set used is presented as Chapter 4.
Chapter 4

LiBr/H\textsubscript{2}O Data Set

Chapter 4 concerns the thermodynamic property data set employed in the present study to generate an analytic Gibbs free energy surface for LiBr/H\textsubscript{2}O. The data set consists of four thermodynamic properties of liquid solutions of LiBr/H\textsubscript{2}O: vapor pressure, isobaric specific heat, density and mean activity coefficient of LiBr in solution. The data were obtained from the chemical and engineering literature.

In Section 4.1 a discussion of smoothed data versus experimental data is presented. In Sections 4.2 to 4.5 the sources of data for the individual properties are discussed. In Section 4.6 weighting assignments made for each of the data types are discussed. The agreement between the literature data and the corresponding property predictions obtained from the free energy surface are discussed subsequently in Chapter 5.

In addition to the four properties included in the data set used to generate the Gibbs free energy surface, data on several other thermodynamic properties were
found in the literature. Calculated values for enthalpy [30,33] and entropy [15,30] of LiBr/H₂O are available. These data could be combined to construct the Gibbs free energy surface and thus provide a means by which the constants in Eq. 2.12 could be evaluated without resort to the multiproperty procedure. However, this procedure would depend heavily on calculated data, some of which has been questioned in the technical literature [11]. The multiproperty approach, used in the current study, provides an independent means to check the accuracy of the previously calculated enthalpy and entropy data. These comparisons are discussed in Chapter 5.

4.1 Smoothed Data

Experimental thermodynamic data on LiBr/H₂O available in the open literature are not sufficient to define all the constants in the Gibbs free energy expression (Eq. 2.12). Accordingly, other kinds of data are required to supplement the experimental data.

The data set used in the present study includes both experimental and smoothed data. The term smoothed data is used here to describe the tabulated data found in the literature that has been interpolated to convenient values of the independent variables. The use
of such smoothed data is unavoidable because insufficient experimental data are found in the literature. Most of the thermodynamic property data on LiBr/H₂O reported in the literature are smoothed data.

The inclusion of smoothed data in the multiproperty least squares procedure formulated in Chapter 3 is governed by the same considerations as the inclusion of experimental data. The dominant consideration is the assignment of appropriate weights to the data points. The assignments are guided by estimates of the standard deviation associated with each data point. Since the standard deviations of the data are not estimated by the experimenters (with one exception discussed in Section 4.6), it was necessary to make standard deviation estimates as a part of this study. Since smoothing algorithms have not been published with the smoothed data tabulations, the standard deviation estimates of this study are necessarily made without regard to the fact that the data have been smoothed. Details of the standard deviation estimation method can be found in Section 4.6.
4.2 Vapor Pressure Data

The present section consists of two subsections. In Section 4.2.1 the vapor pressure data sources are summarized and referenced. In Section 4.2.2 the procedure used for calculating the chemical potential of $\text{H}_2\text{O}$ in the liquid solution from vapor pressure data is discussed.

4.2.1 Vapor Pressure Data Sources

Three sources of LiBr/$\text{H}_2\text{O}$ vapor pressure data are employed in generating the Gibbs free energy surface and are described here briefly. Fedorov et. al. [13] report 35 smoothed data points covering the temperature range 150 → 350 °C and spanning the composition range 0. → 0.56 mass fraction LiBr. Data from this source at temperatures above 250 °C are not included in the least squares calculation because absorption applications are not expected to require properties above this temperature. The high temperature data tended to cause large errors in the low temperature range of interest and was therefore omitted. Boryta et. al. [4] report 32 experimental points obtained by two different methods. These data span the temperature range 0. → 175 °C for LiBr compositions in the range 0.4 → 0.7 mass fraction LiBr.
The third vapor pressure data source is the review by McNeely [33]. Although dew point data are tabulated in the review, these data are simply converted to vapor pressure values by reference to the properties of pure H$_2$O. Dew point temperatures are tabulated over the temperature range 0. → 180. °C and over the composition range of 0. → 0.7 mass fraction LiBr. The tabulated data have been smoothed by an algorithm based on Duhring's Rule [36] which has been found to represent the experimental vapor pressure data from a large number of sources quite accurately. The review encompasses several data sets published previously [22,38]. Only the smoothed values reported by McNeely are included in the least squares calculation.

Vapor pressure data are utilized indirectly in the multiproperty least squares computation to calculate values for the chemical potential of H$_2$O in liquid solutions of LiBr and H$_2$O. The chemical potential data developed is then used directly in the multiproperty least squares computation. The calculation procedure for obtaining the chemical potential of H$_2$O from vapor pressure data is discussed next.
4.2.2 Chemical Potential of H₂O from Vapor Pressure Data

The thermodynamic requirements for a binary system to exist in two-phase equilibrium are that the pressure, temperature and the chemical potential of each component must be equal in both phases. Thus, for vapor/liquid equilibrium, the chemical potential of H₂O must be equal in both the vapor and liquid phases and the chemical potential of LiBr must also be equal in both phases.

For a binary component system in vapor/liquid equilibrium, both the liquid and vapor will, in general, be binary component solutions. However, considerable simplicity in the present analysis can be obtained by approximating the composition of the vapor of LiBr/H₂O as pure H₂O. This assumption is often made when dealing with LiBr/H₂O [15,30,33]. The validity of this assumption, which plays a key role in allowing chemical potential data to be extracted from vapor pressure data, is based on experimental observations. Measurements indicate that the ratio of the vapor pressure of pure H₂O to the vapor pressure of pure LiBr is on the order of 10^{12} at room temperature [12]. The large difference in volatility between the two components justifies the introduction of the approximation mentioned above. It is assumed throughout the present study that the
LiBr/H₂O vapor is pure H₂O. The validity of the approximation is justified by the success of the free energy surface method in reproducing the properties of LiBr/H₂O (Chapter 5).

For pure H₂O vapor, thermodynamic properties are accurately known [233] over a wide range of pressure and temperature. The chemical potential of a substance is equal to the Gibbs free energy expressed on a molar basis. Values for the chemical potential of pure H₂O vapor can be calculated routinely from enthalpy and entropy data for pure H₂O. Once these values are in hand, values for the chemical potential of H₂O in a liquid solution of LiBr and H₂O can be obtained as follows. First, impose the phase equilibrium requirement that the chemical potential of H₂O be equal in the vapor and liquid phases at each of the equilibrium states for which vapor pressure data are available. Then, since the chemical potential of H₂O in the vapor is known (from pure H₂O data at the pressure and temperature obtained from the vapor pressure tabulation), the chemical potential of H₂O in the coexisting liquid is also known directly from the phase equilibrium requirement.

Thus the chemical potential of H₂O in the liquid solution can be calculated from vapor pressure data.
These calculated chemical potential data can be used directly in the multiproperty least squares computation. The primary assumption involved in the use of these data is that the vapor is pure $\text{H}_2\text{O}$.

4.3 Isobaric Specific Heat Data

Five sources of LiBr/$\text{H}_2\text{O}$ specific heat data were found in the literature. Each of these sources is described briefly below. The sources report data over the temperature range $0.\rightarrow 130^\circ\text{C}$ and composition range $0.\rightarrow 0.65$ mass fraction LiBr. The individual data sources are described next.

Eigen and Wicke [113] report 24 experimental values of specific heat at very low LiBr concentrations. Uemura and Hasaba [47] report 33 experimental values over a range of temperature and composition. Lower [30] reports 166 smoothed data points over a similar wide range of temperature and composition. The three sources just referenced were regarded as saturated (vapor/liquid) liquid data in the present study. Parker [37] contributes a detailed review of the available data at 25 $^\circ\text{C}$ and 1 atm. and reports the "best" smoothed values over the entire composition range. Parker's review encompasses the frequently referenced data of Lange and Schwartz [26] and therefore
these data [26] are omitted from the least squares calculation.

The specific heat data available in the sources just referenced is largely saturated liquid data (vapor/liquid equilibrium). In each of the sources with one exception noted below, the specific heat, $c_p$, is tabulated as a function of temperature and composition. Pressure is not explicitly reported, however. This is an important feature for the evaluations of the present investigation because utilization of the specific heat data in the least squares calculation formulated in Chapter 3 requires that the pressure be specified along with the temperature and composition for each data point.

This task of assigning a pressure value at each saturated specific heat data point was addressed by an iterative procedure described below consisting of a sequence of least squares calculations designed to utilize the fact that the data are vapor/liquid equilibrium values. The iterative procedure is required only for the specific heat data specified as vapor/liquid equilibrium data. For the remainder of the specific heat data, the pressure is specified with the data, so calculation of the pressure is unnecessary. The iterative procedure, which was devised as a part of
the present study, is illustrated in the flowchart in Figure 3. The flowchart is discussed next.

The blocks at the top of the flowchart, numbered 1 and 2, represent the data available in the literature. Block 1 represents data for which the pressures are specified in the literature. Block 2 represents the saturated specific heat data for which pressure values are needed. The iterative procedure begins by estimating the vapor pressure for each saturated specific heat data point from published vapor pressure data (see Section 4.2). This step is shown in the flowchart by block 3. The estimated pressures allow the first iteration of the multiproperty least squares computation to proceed. The result, shown by block 4, is a first iteration estimate of the Gibbs free energy surface for LiBr/H$_2$O.

The Gibbs free energy surface is then used to calculate vapor pressures for given values of the temperature and liquid composition, as shown in block 5. This calculation involves equating the chemical potential of H$_2$O in the two equilibrium phases. A unique vapor pressure is determined for each pair of temperature and composition which define the state of the saturated specific heat data points. The vapor pressure estimates that result are then compared with
1. PROPERTY DATA UNAFFECTED BY THE ITERATIVE PROCEDURE
\[ c_p, \rho, \mu_1, \gamma \]

2. VAPOR/LIQUID EQUILIBRIUM DATA
\[ c_p = c_p(T, X) \]

3. INITIAL ESTIMATES OF VAPOR PRESSURES GIVE
\[ c_p = c_p(T, X, p^k) \]

4. MULTIPROPERTY LEAST SQUARES COMPUTATION ==> GIBBS FREE ENERGY SURFACE

5. CALCULATE NEW ESTIMATES OF VAPOR PRESSURES FROM THE GIBBS FREE ENERGY SURFACE
\[ c_p = c_p(T, X, p^k) \]

\[ \sum_{i=1}^{N} (\rho_{i,k} - \rho_{i,k-1.2})^2 < (\text{TOLERANCE})^2 \]

6. STOP

Figure 3: Vapor Pressure Iteration Procedure Flowchart
the vapor pressure estimates from the previous step as shown in block 6. If the two sets of estimates agree within a specified tolerance, then the iterative procedure is terminated. Otherwise, the new vapor pressure estimates become part of the input to the next multiproperty least squares computation.

The iterative procedure involving the vapor pressures is repeated until the vapor pressure estimates at two successive steps agree within a specified tolerance. In the present work, the root mean squared (RMS) difference between the vapor pressures at two successive iterative steps was reduced to less than a tolerance of 1.0 Pa after three multiproperty least squares iterations. This tolerance is less than the level of significance reported in any of the vapor pressure data sources.

The pressures resulting from the iterative procedure agree closely with the initial estimates obtained by interpolation of tabular vapor pressure data. The advantage of the iterative procedure is that it produces results which are consistent, in the least squares sense, with the Gibbs free energy surface derived in this study. Details of the results of the vapor pressure iteration can be found in Section 5.2.
4.4 Density Data

Two sources of LiBr/H₂O liquid density data were found in the literature. The International Critical Tables (ICT) [22] present 214 data points and Uemura and Hasaba [47] present 121 data points. Both data sets encompass similar ranges of temperature: 0 - 100 °C and composition: 0 - 0.65 mass fraction LiBr, and both consist of smoothed data spaced uniformly over the independent variable ranges.

The density data referenced above are regarded as saturated liquid data (vapor/liquid equilibrium). As in the case of the specific heat data just considered, the vapor pressure is not explicitly specified in the tabulations that were found. Accordingly, the iterative procedure described in Section 4.3 provides a method of specifying the vapor pressure for the density data in the manner discussed for the specific heat data. In the case of the density data, 5 iterative steps were required to reduce the RMS difference between the pressures at two successive steps to below 1.0 Pa.
4.5 Mean Activity Coefficient of LiBr Data

The mean activity coefficient of LiBr in aqueous solution at 25 °C and at atmospheric pressure (1.014 bar) has been measured by a number of different investigators. A critical review of these measurements was published by Hamer and Wu [17] in 1972. The review includes a tabulation at 43 compositions. These smoothed data points are included in the multiproperty least squares computation.

The thermodynamic information provided by the mean activity coefficient data is redundant when considered together with the property data specified in Sections 4.2 to 4.4. Furthermore, mean activity coefficient data is available in only a small segment of the range of the independent variables spanned by the other property data. Thus the inclusion of mean activity coefficient data is expected to contribute little to the shape of the Gibbs free energy surface. However, because the underlying experimental work was designed to test fundamental theories of electrolyte solution physics, these data are believed to be accurate, perhaps more so than the other data considered. Therefore, the mean activity data are included in the multiproperty least squares computation.
This concludes the description of the data set. The related topic of data weight assignments is discussed next.

4.6 Data Weight Assignments

The multiproperty least squares formulation presented in Chapter 3 includes a weighting factor for each data point equal to the reciprocal of the standard deviation squared. In the present study, the standard deviation forms the basis of the assignment of data weights. However, the lack of standard deviation specifications with published property data requires that data weights be assigned on the basis of estimates of the standard deviation.

The standard deviation estimates assigned to the property data in this study were obtained in two steps. First, an estimation procedure based on statistical arguments was applied to each individual property data set. The second step involves an assessment of the relative standard deviation (i.e. relative weight) between data sources within each property data set.

The estimation procedure based on statistical arguments is discussed in Section 4.6.1. The assignment of relative weights to the individual data sources is discussed in Section 4.6.2.
4.6.1 Standard Deviation Estimates Based on Statistical Arguments

A major shortcoming of the literature data on LiBr/H₂O is that the standard deviation is rarely mentioned. The mean activity coefficient data set is the only source of data found which includes an estimate of the standard deviation. In that case, a single number is given which is an estimate of the average standard deviation of the reported data. Accordingly, as a part of the present study, an estimate of the standard deviation of the data found in the literature was required. The estimates discussed in the present section assign a single number to the data sets for each property. The number can be viewed as an estimate of the average standard deviation of the individual property data set. The estimation procedure employed here is discussed in detail by Bevington [2]. A brief sketch of the procedure is presented next.

The standard deviation estimation procedure is introduced in terms of the following elementary example. Consider a pair of physical variables such as temperature, T, and the length of a solid rod, L, which have a linear relationship as follows

\[ L = AT + B \] (4.1)
where A and B are constants. Let a set of paired measurements of temperature and rod length be denoted by \((t_i, l_i)\), where \(i\) identifies a particular experiment.

The standard deviation estimation procedure used in this study provides a solution to the problem of estimating from the set of paired measurements the average standard deviation of the length measurements. The procedure rests on the following key assumption. The standard deviations of all the rod length measurements are identical. Symbolically this is stated as follows.

\[
\sigma_{l_i} = \sigma_l \quad (\text{Constant for all } i) \tag{4.2}
\]

The standard deviation estimation procedure, as applied to the rod length measurements, follows. First, a model of the relationship between the measured variables is sought. Motivated by the "known" linear relationship defined in Eq. 4.1 between the physical variables temperature and rod length the following relationship between the respective measured quantities is considered.

\[
l_{pi} = f(t_i; a, b) = at_i + b \tag{4.3}
\]

In Eq. 4.3 the symbol \(l_{pi}\) is introduced to represent the predicted value of the rod length. The constants \(a\) and
b are the most probable least squares estimates of the constants A and B in Eq. 4.1 based on the available data set \((t_i, l_i)\). The determination of the constants \(a\) and \(b\) is discussed next.

The least squares formulation for determining \(a\) and \(b\) in Eq. 4.3 results in the following expression.

\[
\phi = \sum_{i=1}^{N} \left( \frac{f(t_i; a, b) - l_i}{\sigma_{ii}} \right)^2
\]  
\[ (4.4) \]

The function \(\phi\) is to be minimized to obtain values for the constants \(a\) and \(b\).

If \(\sigma_{ii}\) is assumed constant for all \(i\), an alternate form for \(\phi\) which has the same minimum can be written as

\[
\phi_{\text{alt}} = \sum_{i=1}^{N} \left( f(t_i; a, b) - l_i \right)^2
\]  
\[ (4.5) \]

Thus, the constants \(a\) and \(b\) can be determined by minimizing \(\phi_{\text{alt}}\) without knowledge of the value of the standard deviation.

Once the constants in Eq. 4.3 have been determined, the final step in the estimation procedure involves calculating the RMS error between the measured data \(l_i\) and the model prediction \(l_{\text{pi}}\). The standard deviation estimate is equal to the RMS error.
\[ \sigma_1 = \left( \frac{\sum_{i=1}^{N} (l_i - l_{pi})^2}{N} \right)^{1/2} \]  

The standard deviation estimate obtained in Eq. 4.6 is based on the assumption that the standard deviation is constant. When this assumption is valid the method provides a probable estimate of the standard deviation. In actual experiments, where \( \sigma_{1i} \) varies between experiments, the standard deviation estimate resulting from the procedure under discussion can be interpreted as an average standard deviation for the set of experiments.

In summary, the average standard deviation of a measured variable can be estimated from a set of measurements if a model of the dependence of that variable on the other relevant variables is available. For the thermodynamic property data sets considered in this study, the models relating the properties to the independent variables temperature, pressure and composition are derived from the Gibbs free energy expression given by Eq. 2.12. These models allow standard deviation estimates of the property data sets to be determined as discussed next.

Consider, for example, the specific heat data set.
An estimate of the average standard deviation of the specific heat data is needed to establish appropriate weights for these data in the multiproperty least squares computation. The estimation method requires a model of the dependence of specific heat on the temperature, pressure and composition. The model used is the expression for the specific heat derived from the Gibbs free energy expression given by Eq. 2.12. The expression for the specific heat, along with expressions for the other thermodynamic properties considered in this study, can be found in Appendix A.

The average standard deviation of the specific heat data set is estimated by solving a least squares problem based solely on the specific heat data. This results in a set of constants that allow predictions of the specific heat, at particular values of temperature, pressure and composition. The estimate of the average standard deviation of the specific heat data is equal to the RMS error between the actual data and the model predictions.

Thus, estimation of the average standard deviations of each of the individual property data sets (i.e. specific heat, density, chemical potential of H_{2}O and mean activity coefficient of LiBr) requires a separate least squares computation. These computations are
performed prior to the multiproperty least squares computation which depends on their results.

The standard deviation estimates resulting from this procedure are included in Table 1. These estimates are based on the total data set for each property. Also included is the value for the standard deviation of the mean activity coefficient obtained from the literature source [17] as well as an estimate (in parentheses) of the standard deviation of the activity data set made by the method described above. This estimate is provided to demonstrate the level of accuracy possible from the estimation method. Although the values differ by approximately 70%, the estimate provides an accurate guide to the order of magnitude of the standard deviation. The value obtained from the literature data source was used in subsequent calculations. The values in Table 1 form the basis of the data weights used in the multiproperty least squares calculation.

4.6.2 Assignment of Relative Weights within Each Property Data Set

Adjustments to the data weights determined from the standard deviation estimation method discussed in Section 4.6.1 were found to be necessary. They were necessitated due to inconsistencies in both the absolute
Table 1: Standard Deviation Estimates of the LiBr/H₂O Literature Data

<table>
<thead>
<tr>
<th>Property</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Heat - ( C_p )</td>
<td>0.016 J/g-K</td>
</tr>
<tr>
<td>( \text{Range: 1.7 - 4.0 J/g-K} )</td>
<td></td>
</tr>
<tr>
<td>Density - ( \rho )</td>
<td>0.0026 g/cm³</td>
</tr>
<tr>
<td>( \text{Range: 1.0 - 1.8 g/cm³} )</td>
<td></td>
</tr>
<tr>
<td>Chemical Potential of ( \text{H}_2\text{O} ) - ( \mu_1 )</td>
<td>7.7 J/g</td>
</tr>
<tr>
<td>( \text{Range}^{\text{a}}: -728. - 0. J/g )</td>
<td></td>
</tr>
<tr>
<td>Mean Activity Coefficient of LiBr - ( \gamma_1 )</td>
<td>2.0 (1.2)</td>
</tr>
<tr>
<td>( \text{Range: 1.0 - 400.} )</td>
<td></td>
</tr>
</tbody>
</table>

\( \text{a - Relative values; } \mu_1 = 0 \text{ at the triple point of } \text{H}_2\text{O.} \)
accuracy and the variability of the data between sources for a particular property. These adjustments are considered in the present subsection. The reduced weights assigned to certain data sets balance the relative accuracy of the data against the need to include property data over the widest possible range of the independent variables. Thus, data of lower accuracy is included along with the best data to extend the realm of applicability of the final result.

Extensive analysis of the data set, based on the methods described in Section 4.6.1, led to estimates of the relative standard deviation or relative weight of the data from separate sources for a particular property. These estimates form the basis of choices of relative weights for the data sources within each property data set. The final adjustments were made empirically by varying the weights on the data and examining the effect on the overall correlation of the data. Particular emphasis was placed on achieving an accurate reproduction of the McNeely vapor pressure data since this data set is widely accepted in the absorption industry. The results of this extensive analysis, which included many trial solutions of the multiproperty least squares problem, are discussed in this subsection.

The end results of the data analysis are included
### Table 2: Relative Weighting of the LiBr/H$_2$O Data Sources

<table>
<thead>
<tr>
<th>Data Set</th>
<th>Number of Points</th>
<th>Relative Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Specific Heat</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uemura</td>
<td>26</td>
<td>0.1</td>
</tr>
<tr>
<td>Eigen</td>
<td>21</td>
<td>1.0</td>
</tr>
<tr>
<td>Lower</td>
<td>166</td>
<td>1.0</td>
</tr>
<tr>
<td>Parker</td>
<td>23</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ICT</td>
<td>160</td>
<td>0.33333</td>
</tr>
<tr>
<td>ICT</td>
<td>51</td>
<td>1.0</td>
</tr>
<tr>
<td>Uemura</td>
<td>118</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>Chemical Potential of H$_2$O</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fedorov</td>
<td>21</td>
<td>0.194</td>
</tr>
<tr>
<td>Boryta</td>
<td>26</td>
<td>0.966</td>
</tr>
<tr>
<td>McNeely</td>
<td>206</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>Activity Coefficient of LiBr</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hamer</td>
<td>43</td>
<td>1.0</td>
</tr>
</tbody>
</table>
in Table 2 as relative weights. A relative weight of 1.0 means that the data weight is equal to the reciprocal of the standard deviation, reported in Table 1, squared. Thus, the standard deviation estimates contained in Table 1 form the basis of the data weights. Relative weights less than 1.0 decrease the influence of that data by a factor equal to the relative weight. Thus the weighting factors, \( w \), used in the multiproperty least squares computation take the form

\[
w = \frac{w_{\text{rel}}}{\sigma^2}
\]

where \( w_{\text{rel}} \) is the relative weight and \( \sigma \) is the standard deviation estimate.

The specific heat data of Uemura and Hasaba was found to be inconsistent with the other three specific heat data sources. The relative weight of 0.1 for this data source balances the influence of the four data sets. This choice is equivalent to assigning a standard deviation to the Uemura and Hasaba data 3.16 times larger than the standard deviation assigned to the other specific heat data.

The two density data sources were found to be highly consistent. The relative weight of 1/3 assigned
to 160 of the ICT data points is designed to avoid emphasizing one data set just because it provides more data points. Thus, this weighting choice was based on the goal of equal influence for each density data source. Because of the high consistency between the two data sources, this weighting choice has very little effect on the Gibbs free energy surface.

The chemical potential of $H_2O$ was calculated from vapor pressure data. The three vapor pressure data sources were found to be somewhat inconsistent. In particular, the Fedorov data source was found to deviate from the other two sources. Thus the relative weights indicated in Table 2 were assigned to balance the influence of the data sources with major emphasis placed on the McNeely data set.

4.7 Closure

The ultimate justification for the standard deviation estimates and the relative weight assignments must be inferred from the ability of the Gibbs free energy surface which is subsequently developed to represent the properties of LiBr/$H_2O$. The weighting scheme described in this chapter results in excellent reproduction of the input data as well as good agreement with thermodynamic properties calculated using other
methods. These topics are discussed in detail in Chapter 5.
Chapter 5

A Gibbs Free Energy Surface For LiBr/H₂O

The implementation of the multiproperty least squares computation, which defines a Gibbs free energy surface for LiBr/H₂O, is reviewed in the present chapter along with a discussion of the results of the computation. The formulation of the least squares problem is the subject of Chapter 3 and the data set used in the least squares computation is discussed in Chapter 4.

The present chapter is divided into 7 sections concerning the following topics. In Section 5.1 the details of the computation are briefly discussed. Section 5.2 presents the results of a comparison of the three candidate functional forms introduced in Section 2.4 for the temperature and pressure dependence of the empirical terms in the Gibbs free energy expression. In Sections 5.3 to 5.5 comparisons between literature property data and property values derived from the Gibbs free energy surface are discussed. In Section 5.6 accuracy estimates for the derived
thermodynamic properties are presented and discussed. Finally, in Section 5.7 a summary of the LiBr/H₂O property work discussed in Chapters 2 to 5 is presented.

5.1 The Multiproperty Least Squares Computation

The details of the multiproperty least squares computation are briefly considered in this section. The discussion begins by identifying several parameters which provide insight into the complexity of the computation. The solution method chosen is then discussed. The computer and programming language used in the present study are described and computational accuracy and dynamic range considerations are discussed. The computation time requirements are also noted.

Solution of the multiproperty least squares problem formulated in Chapter 3 requires two major steps. First the minimization problem, represented by Eq. 3.11, must be reformulated into a set of k simultaneous linear equations in the k undetermined constants. Secondly, the set of equations must be solved for the set of constants. These steps are discussed next in more detail.

Reformulation of the minimization problem yields a set of equations which can be represented by the following matrix equation
where \( A \) is a \( k \times k \) matrix and \( y \) and \( z \) are vectors with \( k \) components. The elements of the matrix \( A \) can be determined by applying standard calculus minimization methods [2] to the function \( \phi \) in Eq. 3.11. The result can be written as

\[
A_{ij} = \sum_{i=1}^{k} \frac{\partial^2 \phi}{\partial y_i \partial y_j} + \sum_{i=1}^{k} \frac{\partial^2 \phi}{\partial y_i \partial y_j}
\]

The vector \( z \) is composed of the elements

\[
z_m = \sum_{i=1}^{k} \frac{\partial \phi}{\partial y_i} (\mu_{ri} - f_{cio})
\]

The indices \( m \) and \( n \) in Eqs. 5.2 and 5.3 assume the values from 1 to \( k \). The functions, denoted \( f \), which appear in the partial derivatives in Eqs. 5.2 and 5.3
are defined in Eqs. 3.7 to 3.10. Note that the partial derivatives are taken with all of the remaining undetermined constants held fixed. The subscript 0, on the functions denoted \( f \), indicates the constant component of the function. The constant component can be calculated by setting all the \( y \)'s to zero. The summation limits \( l, q, t \) and \( u \) refer, respectively, to the number of data points available for the properties specific heat, density, chemical potential of \( H_2O \) and mean activity coefficient of LiBr.

The total number of data points used is 869 which equals the sum of \( l, q, t \) and \( u \). The final form chosen for the Gibbs free energy involves 37 constants. Thus \( k \) is equal to 37. These figures give an indication of the complexity of the calculation: 37 adjustable constants are determined using 869 data points.

After the matrix and resultant vector elements have been calculated by evaluating Eqs. 5.2 and 5.3, the solution for the undetermined constants, \( y_i, i=1,...,37 \), is relatively straightforward. The method chosen in this study is a standard Gaussian elimination with pivoting on the maximum elements [45]. This method minimizes the numerical truncation error.

The computations were performed on a Digital Equipment Corporation VAX-11/750 with a floating point
accelerator. The routines were written in VAX-11 FORTRAN V3.5-62 and they were executed under the VMS V3.6 operating system. All floating point operations were performed in double precision. This provides at least 15 decimal digits of precision and a dynamic range of approximately $0.29 \times 10^{-38}$ through $1.7 \times 10^{38}$ [48].

The computations were performed in double precision because it was found that single precision computations in the matrix equation solution can lead to significant errors. Single precision provides a precision of at least 6 decimal digits. Errors due to truncation were reduced significantly by the use of double precision. Double precision is the highest precision level readily available on the chosen computing system.

In early attempts to complete the least squares computation, the Gaussian elimination routine included an incidental calculation of the determinant of the coefficient matrix $A$, defined in Eq. 5.1. This calculation had to be abandoned in subsequent attempts because the value of the determinant is greater than the largest number that the computer can represent ($1.7 \times 10^{38}$). After this calculation was eliminated, no other dynamic range problems were encountered in the computation.

The multiproperty least squares computation
required approximately 12 minutes of central processing unit (CPU) time. The majority of this time is spent generating the elements of the coefficient matrix and the resultant vector. The Gaussian elimination requires only approximately 30 seconds of CPU time. The most time consuming portion of the entire computation is the portion spent calculating the pure $H_2O$ properties for each data point. This calculation requires an iterative solution for the density from the Steam Table equations [231].

5.2 Comparison of the Three Candidate Formulations

Introduced in Section 2.4

Three candidate functional forms for the temperature and pressure dependence of the empirical terms in the Gibbs free energy expression are given by Eqs. 2.13 to 2.18. These candidates are evaluated in this section and the best candidate determined. The best candidate is defined as the one that exhibits the highest squared multiple correlation coefficient for the full data set.

Table 3 summarizes results obtained with the three candidates. Each of the entries in Table 3 is a squared multiple correlation coefficient. The entries in the bottom row represent the squared multiple correlation coefficient of the full data set including each of the
Table 3: Squared Multiple Correlation Coefficients ($R^2$) of the Three Candidate Formulations

<table>
<thead>
<tr>
<th>LiBr/$H_2O$ Data Set</th>
<th>Candidate</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Heat</td>
<td>0.99347</td>
<td>0.99608</td>
<td>0.99575</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>0.99918</td>
<td>0.99981</td>
<td>0.99977</td>
<td></td>
</tr>
<tr>
<td>Chemical Potential of $H_2O$</td>
<td>0.99769</td>
<td>0.99874</td>
<td>0.99873</td>
<td></td>
</tr>
<tr>
<td>Mean Activity Coefficient of LiBr</td>
<td>0.99908</td>
<td>0.99904</td>
<td>0.99906</td>
<td></td>
</tr>
<tr>
<td>Full Data Set</td>
<td>0.99940</td>
<td>0.99967</td>
<td>0.99966</td>
<td></td>
</tr>
</tbody>
</table>
four individual property data sets. Candidate number 2 can be seen to be the best formulation although candidate number 3 also represents the full data set well. Candidate number 1 exhibits a value of $R^2$ somewhat lower than the other two formulations and is correspondingly inferior to the other formulations in reproducing the input data.

These conclusions are generally supported by the squared multiple correlation coefficient values for the individual property data sets which are also given in Table 3. For the specific heat, density and chemical potential of H$_2$O data sets, candidate number 2 exhibits higher correlation of the data than either of the other two candidates. However, for the activity coefficient of LiBr data set, candidate number 2 exhibits the lowest correlation of the three candidates. The differences between the three candidates are small in this case. Therefore, although the use of candidate number 2 sacrifices some correlation of the activity data, its use achieves the best correlation of the full data set. With these considerations candidate number 2 was chosen as the best formulation. The results which follow are based on this choice.
5.3 Vapor Pressure Iteration Results

The purpose of the vapor pressure iteration is discussed in Section 4.2. As a part of that discussion, a flowchart of the iteration procedure is presented as Figure 3 on page 85. To summarize briefly, the vapor pressure iteration provides a means by which vapor pressure values can be calculated for vapor/liquid equilibrium data points for which no pressures are tabulated in the literature. Much of the specific heat data and all of the density data found for LiBr/H₂O fall into this category. Therefore, the use of these data requires an estimate of the vapor pressures. The vapor pressure iteration method, the results of which are presented in this section, provides vapor pressure estimates which are consistent with the derived Gibbs free energy surface and consistent with the total data set in the least squares sense.

Table 4 summarizes the vapor pressure iteration numerical results. At each iteration, the vapor pressure predictions from the previous iteration become the input data, along with the remainder of the property data which are unaffected by the iteration procedure. Each iteration consists of a multiproperty least squares computation. The first iteration required vapor
Table 4: Vapor Pressure Iteration Results - Root Mean Squared Error Between the Input Data and the Gibbs Free Energy Surface Derived Values (Units : Pa)

<table>
<thead>
<tr>
<th>Iteration Number</th>
<th>Equilibrium Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Specific Heat $^a$</td>
</tr>
<tr>
<td>1$^b$</td>
<td>6173.</td>
</tr>
<tr>
<td>2</td>
<td>2.937</td>
</tr>
<tr>
<td>3</td>
<td>0.2757</td>
</tr>
<tr>
<td>4</td>
<td>0.01036</td>
</tr>
<tr>
<td>5$^c$</td>
<td>0.008445</td>
</tr>
</tbody>
</table>

$^a$ - Entries are the root mean squared error between the input vapor pressure estimates and the corresponding values derived from the Gibbs free energy surface (Units : Pa)

$^b$ - The first iteration required vapor pressure estimates for each of the equilibrium specific heat and density data points. These initial estimates were obtained from the vapor pressure data set.

$^c$ - The iteration procedure was terminated after 5 iterations because the RMS error was reduced to below the tolerance of 1.0 Pa for both data sets.
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pressure estimates from an independent source. As discussed in Section 4.2, the initial vapor pressure estimates were obtained by interpolation using the vapor pressure data set.

The convergence of the iterative procedure can be clearly seen by an examination of Table 4. The initial vapor pressure estimates for the specific heat data set are significantly better than the corresponding estimates for the density data set. At the first iteration, the RMS error associated with the density data set is approximately 10 times greater than the RMS error associated with the specific heat data set. An examination of the causes for this discrepancy is discussed next.

The large discrepancy between the RMS errors for the specific heat and the density data sets at the first iteration can be traced to the method used to obtain the initial estimates of the vapor pressures. This method involves a two step linear interpolation between vapor pressure values tabulated versus temperature and composition.

The effects of interpolation error were smaller for the specific heat data set because the specific heat data points correspond quite closely with vapor pressure data points. In other words, for many of the specific
heat data points no interpolation was necessary because the tabulated data coincided with tabulated vapor pressure data (tabulated at identical temperatures and compositions). This coincidence was not found for the density data set. For the density data, the majority of the data points required interpolation. Thus the effects of interpolation error are more pronounced for the density data set than for the specific heat data set.

The iterative procedure exhibits rapid convergence. The accuracy of the initial vapor pressure estimates can be observed to influence each iteration but its effects are largely damped after 5 iterations. At the fifth iteration the RMS error associated with the density data set is only 3 times greater than the RMS error associated with the specific heat data set. The iteration process was terminated when the RMS errors dropped below 1.0 Pa. This level of error in the vapor pressures is well below the level of significance reported in any of the vapor pressure data sources found in the literature.
5.4 Comparisons of Derived Properties with Input Data

As discussed previously in Chapters 3 and 4, four individual thermodynamic property data sets form the input to the multiproperty least squares computation. The discussion in this section focuses on the ability of the derived Gibbs free energy surface to reproduce the input data.

Table 5 is a statistical summary of the comparisons between the derived properties and the input data. For each of the four properties, statistical comparisons are made with the total data set for that property and with the individual data sources. The statistical measures used are defined in Section 3.3. The number of data points and the relative weights within each data set are identical to those appearing in Table 2 and are repeated here for completeness.

For each individual property, the range of values of that property found in the literature is specified in the heading. This information helps clarify the meaning of the statistical measures in some cases. A discussion of the statistics for each property follows.

Although the specific heat data set exhibits the lowest squared multiple correlation coefficient ($R^2$) of all the individual property data sets, the accuracy of
Table 5: Statistical Comparison of the Gibbs Free Energy Surface Derived Data with the Input Data

<table>
<thead>
<tr>
<th>Weighted Weighted</th>
<th>2</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBr/H₂O Number</td>
<td>Error</td>
<td>Error</td>
</tr>
<tr>
<td>Specific Heat (Range : 1.7 → 4.0 J/g-K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eigen</td>
<td>0.015941</td>
<td>0.018481</td>
</tr>
<tr>
<td>Lower</td>
<td>0.0035112</td>
<td>0.030938</td>
</tr>
<tr>
<td>Parker</td>
<td>-0.050518</td>
<td>0.077057</td>
</tr>
<tr>
<td>Uemura</td>
<td>0.16590</td>
<td>0.20289</td>
</tr>
<tr>
<td>TOTAL</td>
<td>0.00088002</td>
<td>0.043899</td>
</tr>
</tbody>
</table>

Density (Range : 1.0 → 1.8 g/cm³) |  |
| ICT | 0.00078043 | 0.0018538 | 0.99953 | 0.33 | 160 |
| ICT | 0.0025255 | 0.003801 | 0.99949 | 1.0 | 51 |
| Uemura | 0.0014102 | 0.0030502 | 0.99977 | 1.0 | 118 |
| TOTAL | 0.000012193 | 0.0030045 | 0.99981 | 329 |
Table 5: (continued)

<table>
<thead>
<tr>
<th>Data Set</th>
<th>Weighted Mean</th>
<th>Weighted RMS Error</th>
<th>$R^2$ Relative of Weight</th>
<th>Number of Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fedorov</td>
<td>5.2781</td>
<td>10.820</td>
<td>0.99272</td>
<td>0.194</td>
</tr>
<tr>
<td>Boryta</td>
<td>-5.1097</td>
<td>12.548</td>
<td>0.98863</td>
<td>0.966</td>
</tr>
<tr>
<td>McNeely</td>
<td>-0.51354</td>
<td>5.1868</td>
<td>0.99924</td>
<td>1.0</td>
</tr>
<tr>
<td>TOTAL</td>
<td>-0.90403</td>
<td>6.5120</td>
<td>0.99874</td>
<td></td>
</tr>
</tbody>
</table>

Chemical Potential of $H_2O$ (Range : $-728.0 \rightarrow 0. J/g$)

Mean Activity Coefficient of LiBr (Range 1. $\rightarrow$ 400.)

<table>
<thead>
<tr>
<th>Hamer</th>
<th>0.83802</th>
<th>3.504</th>
<th>0.99904</th>
<th>1.0</th>
<th>43</th>
</tr>
</thead>
</table>
the derived specific heat values, as measured by the other statistics, is high. The weighted RMS error between the derived values and the input data is approximately 1.5% of the average specific heat magnitude (2.85 J/g-K). The weighted mean error is approximately 0.03% of the average specific heat magnitude.

The contribution to the mean and RMS error statistics of each data source for specific heat can be read from Table 5. The majority of the data is reproduced with excellent accuracy. However, the Uemura specific heat data set is reproduced with significantly less accuracy than the other data. The factors affecting the accuracy of reproduction of the Uemura specific heat data set are discussed next.

Since both the Uemura and Lower specific heat data sets span similar wide ranges of the independent variable space, the following examination of the specific heat data focuses on a comparison of the Uemura and Lower data sets. Preliminary data analysis suggested inconsistency between the Uemura and Lower data sets (see Section 4.6.2). Specifically, a significant difference exists in the standard deviation estimates between the two sets. The preliminary data analysis resulted in the assignment of the relative
weights listed in Table 5. The Uemura data set was
given less weight than the Lower data set because the
data analysis indicated significantly higher data
variability or scatter compared with the Lower data. No
information about the mean differences between the two
data sets was available from the preliminary analysis,
however.

The results in Table 5 show a substantial
difference between the mean errors of the Uemura and
Lower specific heat data sets. For the Uemura data set
the weighted mean error is 0.1659 J/g-K whereas for the
Lower data set it is 0.0035112 J/g-K. The difference,
0.1624 J/g-K, represents approximately 5.7% of the
average specific heat magnitude. Following from the
definition of the weighted mean and weighted RMS errors
in Eqs. 3.14 and 3.15, the RMS error is always greater
than the mean error. A measure of the variability of
the data sets is the difference between the RMS error
and the mean error. With this measure the mean error
effects are eliminated and only the variability about
the mean is measured. Using this measure, both the
Uemura and the Lower specific heat data sets exhibit
comparable variability. Thus the striking difference
between the two data sets is the difference between the
mean errors. Conclusions based on this analysis are
discussed next.
The analysis method used in this study shows clearly that the Uemura and Lower specific heat data sets are inconsistent. However, the analysis does not allow a decision as to which data set is more accurate. The accuracy specification for specific heat in Section 5.6 reflects this uncertainty.

The Lower specific heat data set was emphasized in the present study over the Uemura data set primarily because the Lower data set (1) contains a larger number of points and (2) forms the basis of the widely used McNeely enthalpy data set as well as Lower's own enthalpy data set. The preliminary data analysis leading to the data weights was skewed by the preponderance of data points supplied by the Lower data set. The multiproperty least squares computation was similarly skewed toward emphasis of the Lower data set by the data weights and the number of data points. Thus, the fact that the Gibbs free energy surface reproduces the Lower data set more closely than the Uemura data set is not surprising.

The density data set exhibits the highest squared multiple correlation coefficient of all the individual property data sets. This indication of high correlation is also evident in the calculated error statistics. The weighted RMS error is approximately 0.2% of the average
density magnitude \(1.4 \text{ g/cm}^3\). The weighted mean error is approximately 0.0008\% of the average density magnitude. The density errors are approximately 10 times less than the specific heat errors when expressed as a fraction of the magnitude. The difference can be attributed to the superior quality of the density data as compared to the specific heat data. This difference is observable in the standard deviation estimates for those data sets given in Table 1.

The two density data sources exhibit high consistency with each other. The difference in the weighted mean error for each source is within the weighted RMS error of each. Thus, all the density data can be reproduced accurately with the derived Gibbs free energy surface.

The vapor pressure data set is described statistically in Table 5 from the perspective of the least squares computation. From this perspective, the chemical potential of \(\text{H}_2\text{O}\), which is calculable from the vapor pressure as described in Section 4.2, is the relevant quantity. A direct comparison of the derived vapor pressure values with the literature data is made subsequently in Table 6 (page 124) accompanied by a discussion.

For the chemical potential of \(\text{H}_2\text{O}\), it is not
meaningful to express errors as percentages of the magnitude because the magnitude of the chemical potential is dependent on the choice of datum states (for further discussion of datum states see Section 5.5). The choice of datum states affects the magnitude of the chemical potential at a given state but has no effect on the error statistics in Table 5. Therefore these error statistics are difficult to interpret as indicators of the quality of correlation of the chemical potential data set because no absolute magnitude scale is obvious. However, high correlation is suggested by the squared multiple correlation coefficient.

Some inconsistency between the individual chemical potential data sets was found in preliminary data analysis. This analysis led to the relative weights tabulated in Table 5. These inconsistencies are reflected in the differences between the weighted mean and the weighted RMS errors of the individual data sets. The McNeely data is reproduced to much better accuracy than either of the other two data sets. This is expected because the McNeely data set contributes the majority of the data points.

The mean activity coefficient data set also exhibits a high squared multiple correlation coef-
Thus reasonable reproduction of the activity data can be obtained. For this data set the weighted mean and weighted RMS errors are difficult to interpret because the magnitude of the mean activity coefficient has such a large range (1. \( \rightarrow \) 400.). Separate calculations of the error, compared to the magnitude of the activity coefficient for each data point, indicate the average error is -2.3% and the maximum error is +36%.

The maximum fractional error for the activity data is quite large. One contributing factor to the lack of accuracy in reproduction of the activity coefficient data is the choice, discussed in Section 5.2, of the pressure and temperature dependence of the empirical terms in the Gibbs free energy expression. Some activity coefficient accuracy was sacrificed to obtain better reproduction of the other properties. Another contributing factor is believed to be insufficient degrees of freedom in the composition dependence of the Gibbs free energy expression (Eq. 2.12). This claim is supported by the correlation work done by Hamer and Wu [17] in which terms involving molality up to the sixth power were included. The expression used in the present study only utilizes terms up to molality squared. For the present purpose of thermodynamic
property calculations for absorption system analysis, the observed shortcoming in activity coefficient accuracy is tolerable because activity coefficient values are not needed in a typical analysis. Accurate correlation of all the available data including the activity coefficient data would require additional terms and constants in the Gibbs free energy expression, and is left to future investigation (see Chapter 7).

Table 6 provides a statistical comparison between the vapor pressure data and the vapor pressures derived from the Gibbs free energy surface. Several features of the comparison are notable. The squared multiple correlation coefficient clearly indicates a high level of correlation of the vapor pressure data. The Fedorov data set exhibits significantly larger weighted mean and weighted RMS error statistics than the other two data sources. This is expected since the Fedorov data set was assigned a low relative weight (see Table 5) and is consistent with the trends exhibited by the chemical potential data set in Table 5. These statistics are skewed somewhat by the fact that the Fedorov data spans a higher temperature range than either of the other two data sets. Thus the Fedorov vapor pressures are significantly larger than those of the other data sets. Expressing the error at each data point as a fraction of
Table 6: Statistical Comparison of the Gibbs Free Energy Surface Derived Vapor Pressure with Vapor Pressure Data

<table>
<thead>
<tr>
<th>Data Set</th>
<th>Weighted Mean</th>
<th>Weighted RMS Error</th>
<th>Mean $R^2$</th>
<th>Fractional Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>McNeely$^a$</td>
<td>-0.00021193</td>
<td>0.020789</td>
<td>0.99849</td>
</tr>
<tr>
<td></td>
<td>Boryta$^b$</td>
<td>0.0028306</td>
<td>0.019384</td>
<td>0.99320</td>
</tr>
<tr>
<td></td>
<td>Fedorov$^c$</td>
<td>-0.22098</td>
<td>0.84964</td>
<td>0.99442</td>
</tr>
<tr>
<td></td>
<td>TOTAL</td>
<td>-0.0037112</td>
<td>0.11368</td>
<td>0.99756</td>
</tr>
</tbody>
</table>

Individual Vapor Pressure Data Set Ranges:

- a - 0.0021 → 2.0 bar
- b - 0.018 → 0.83 bar
- c - 1.1 → 38. bar
the absolute pressure and averaging over all the data points yields values for the mean fractional error. From this perspective, the Fedorov and Boryta data sets exhibit errors of similar magnitude.

In addition to the statistical comparisons just discussed, three tables are provided next which compare the literature data against the properties calculated from the Gibbs free energy surface at selected state points. Table 7 compares the vapor pressure data of McNeely [33] against the calculated values. Similarly, Table 8 compares the Lower [30] specific heat data against the calculated values. Finally, Table 9 compares the ICT [22] density data against the calculated values. In accordance with the statistical measures provided previously, these comparisons show good agreement between input and calculated data.

Overall, the input data can be reproduced with excellent accuracy. The density is reproduced with the highest accuracy while the specific heat reproduction exhibits the lowest accuracy as measured by the squared multiple correlation coefficients. The results of the present section demonstrate that the input data can be accurately reproduced. The next section examines the ability of the Gibbs free energy expression to reproduce two properties that were not used as input data.
Table 7: LiBr/H₂O Vapor Pressure Comparison

<table>
<thead>
<tr>
<th>p* (bar)</th>
<th>McNeely [33]</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>T=50 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xₘₐₓ =0.2</td>
<td>0.10541</td>
<td>0.10715</td>
</tr>
<tr>
<td></td>
<td>0.062684</td>
<td>0.065923</td>
</tr>
<tr>
<td></td>
<td>0.012449</td>
<td>0.012161</td>
</tr>
<tr>
<td>T=100 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xₘₐₓ =0.2</td>
<td>0.86912</td>
<td>0.88675</td>
</tr>
<tr>
<td></td>
<td>0.56018</td>
<td>0.57154</td>
</tr>
<tr>
<td></td>
<td>0.14146</td>
<td>0.14101</td>
</tr>
</tbody>
</table>

* - Vapor pressures calculated from the Gibbs free energy surface.
**Table 8: LiBr/H₂O Specific Heat Comparison**

<table>
<thead>
<tr>
<th></th>
<th>$c_p$ (J/g-K)</th>
<th>Lower [30] % Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_p^*$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>T=50 °C</strong></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_m = 0.2$</td>
<td>3.2867</td>
<td>3.2906</td>
</tr>
<tr>
<td>0.4</td>
<td>2.5206</td>
<td>2.4952</td>
</tr>
<tr>
<td>0.6</td>
<td>1.9032</td>
<td>1.9593</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>T=100 °C</strong></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_m = 0.2$</td>
<td>3.3138</td>
<td>3.3241</td>
</tr>
<tr>
<td>0.4</td>
<td>2.5472</td>
<td>2.5203</td>
</tr>
<tr>
<td>0.6</td>
<td>1.9753</td>
<td>2.0179</td>
</tr>
</tbody>
</table>

* - Values calculated from the Gibbs free energy surface derived in the present study
<table>
<thead>
<tr>
<th>$X_m$</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>ICT [22]</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1.1490</td>
<td>1.14936</td>
<td>0.03</td>
</tr>
<tr>
<td>0.4</td>
<td>1.3712</td>
<td>1.36869</td>
<td>-0.18</td>
</tr>
<tr>
<td>0.6</td>
<td>1.7012</td>
<td>1.69853</td>
<td>0.16</td>
</tr>
<tr>
<td>0.2</td>
<td>1.1206</td>
<td>1.1210</td>
<td>0.04</td>
</tr>
<tr>
<td>0.4</td>
<td>1.3449</td>
<td>1.3404</td>
<td>-0.33</td>
</tr>
<tr>
<td>0.6</td>
<td>1.6708</td>
<td>N.V.</td>
<td>-</td>
</tr>
</tbody>
</table>

* - Values calculated from the Gibbs free energy surface derived in the present study

N.V. - No value reported
5.5 Comparisons with Enthalpy and Entropy Data

The topic of this section is the accuracy of the enthalpy and entropy values derived from the Gibbs free energy surface. Comparisons with the available calculated literature data are made. These comparisons require that a consistent choice of enthalpy and entropy datums be made for each data set considered. The subject of datum states is considered next.

5.5.1 Datum States

The enthalpy and entropy data found in the literature are based on several different choices of datum states. For meaningful comparisons between data sets, each data set must be expressed relative to a common choice of datum states. Simple algorithms for correcting the various data sets to the datum states used in the present study are included in Table 10. The algorithms define a correction, dependent on composition, that must be added to the data. The corrections are expressed in the originally published units for clarity. Unit conversion is the final step in preparing the data sets for comparison.

The specification of the enthalpy and the entropy for the binary system LiBr/H₂O involves two datum
<table>
<thead>
<tr>
<th>Data Set</th>
<th>Units</th>
<th>Correction Added to the Data</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Enthalpy</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>McNeely</td>
<td>Btu/lbm</td>
<td>None</td>
</tr>
<tr>
<td>Lower</td>
<td>cal/g</td>
<td>$-100. + 106.8 , X_m$</td>
</tr>
<tr>
<td><strong>Entropy</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower</td>
<td>cal/g-K</td>
<td>$-0.813 + 0.652 , X_m$</td>
</tr>
<tr>
<td>Gupta</td>
<td>J/g-K</td>
<td>$-0.1294 , X_m$</td>
</tr>
</tbody>
</table>

$X_m$ - mass fraction LiBr
states. The requirements for the choice of useful datum states are that the two states be unambiguous and readily reproducible and that the two states exist at different compositions. Note that pure component datum states, which are usual choices for many binary component systems, are not used for LiBr/H₂O. This is because pure LiBr exists as a solid in the temperature and pressure range of interest and this complicates the specification of properties of its liquid aqueous solutions.

The datum states utilized in the present study are as follows. One datum state is pure H₂O at the state chosen by Keenan et. al. [23]. This choice is the triple point of H₂O (273.16 K, 0.006113 bar). In this state, the specific internal energy and the specific entropy are assigned values of zero. With this choice of datum state, the specific enthalpy of pure H₂O has a value of approximately 0.02 J/g at the triple point. For the second datum state, the specification is a liquid solution of LiBr/H₂O with a composition of 0.5 mass fraction LiBr, a temperature of 273.15 K and a pressure of 0.0013614 bar. This is a saturated (vapor/liquid) state. The specific enthalpy and specific entropy of the solution are assigned values of zero at this datum state. This defines the values for h₂₀° and s₂₀° found in Appendix A.
The foregoing datum states for LiBr/H₂O are also used by McNeely [33]. The choice of these states allows the specific enthalpy and entropy in a given state to be calculated relative to the datum states. Note that the choice of datum states has no effect on first and second law analyses which require only differences in enthalpy and entropy.

5.5.2 Data Comparisons

Table 11 provides a statistical comparison between the enthalpy and entropy values derived from the Gibbs free energy surface and the available literature data which are calculated by other means. The statistics included are calculated as defined in Eqs. 3.14 to 3.17 except that in the present case each data point is assigned a weight of unity (i.e. \( w_i = 1 \) for all \( i \)). The mean and RMS errors are expressed in the units indicated for the range.

Comparison with the two enthalpy data sources shows substantial agreement as indicated by high values of the squared multiple correlation coefficient. Comparable values for the mean and RMS errors for the two data sets implies that the two data sets agree with each other.

A graphical comparison of the specific enthalpy along selected isotherms is presented in Figure 4. The
Table 11: Statistical Comparisons of the Gibbs Free Energy Surface Derived Enthalpy and Entropy with Literature Data

<table>
<thead>
<tr>
<th>Data Set</th>
<th>Mean Error</th>
<th>RMS Error</th>
<th>$R^2$</th>
<th>Number of Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mcneely</td>
<td>1.3447</td>
<td>6.4801</td>
<td>0.99800</td>
<td>171</td>
</tr>
<tr>
<td>Lower</td>
<td>5.8168</td>
<td>8.1359</td>
<td>0.99553</td>
<td>176</td>
</tr>
</tbody>
</table>

Enthalpy (Range*: -30. → 680. J/g)

<table>
<thead>
<tr>
<th>Entropy (Range*: 0. → 1.6 J/g-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower</td>
</tr>
<tr>
<td>Gupta</td>
</tr>
</tbody>
</table>

* - Ranges reflect datum state choices discussed in Section 5.2.1.
solid lines represent the values derived from the Gibbs free energy surface. The McNeely data is denoted by circles and the Lower data is denoted by triangles.

The generally good agreement shown by Figure 4 is less satisfactory at lower temperatures. This is believed to be as a result of several factors. One factor is that the accuracy of a least squares correlation frequently degrades near the edges of the input data set. Poor extrapolation capabilities often accompany the degradation. Another factor is that the enthalpy calculation method used in the present study utilizes as input a significantly larger data base than the calculation methods of McNeely and Lower. Thus the results of this study are expected to be less sensitive to localized data errors. The overall good agreement between the literature data and the Gibbs free energy surface predictions suggest that the Gibbs free energy surface predictions would serve as the standard of comparison.

Similar comparisons with the two entropy data sources also yield high values for the squared multiple correlation coefficients (Table 11). Thus, generally good agreement exists between the entropy values derived from the Gibbs free energy surface and the literature data. This good agreement is also indicated by the
Figure 4: LiBr/H$_2$O Enthalpy Comparison
error statistics. A graphical comparison of the specific entropy along selected isotherms is presented in Figure 5. The Lower data is denoted by triangles and the Gupta data is denoted by circles. The graph shows that the general trends of the data are well represented and that the Gibbs free energy surface agrees more closely with the data of Lower than with the data of Gupta.

The generally good agreement of the calculated entropy values with the literature data can be seen to be somewhat less satisfactory at lower temperatures. A similar trend was also observed for the enthalpy data discussed previously. The contributing factors mentioned in the enthalpy discussion are also relevant to the entropy data. As an additional contributing factor to the entropy discrepancy it can be mentioned that previous entropy calculation methods, such as those used by Gupta and Lower, depend directly on calculated enthalpy data. Thus, errors in the enthalpy calculation might cause errors in the entropy values. This explanation is consistent with the observed discrepancies between the present calculations and those conducted by Gupta and Lower because the major discrepancies in both enthalpy and entropy occur in the same region of the temperature-composition space. The
Figure 5: LiBr/H$_2$O Entropy Comparison
good overall agreement with the results of the present study which the Gupta and Lower entropy data sets exhibit is further evidence that the present work accurately represents LiBr/H₂O.

5.5.3 Enthalpy and Entropy Plots

The Gibbs free energy surface derived in this study provides a convenient means of examining many aspects of the thermodynamic properties of LiBr/H₂O. For absorption system design purposes, it is convenient to have information about the enthalpy and entropy along isobars as well as isotherms. Figures 6 and 7 display, respectively, the enthalpy and entropy along selected isotherms (solid lines) and isobars (dashed lines). One of the benefits of the free energy surface method is that the resulting expression can be readily manipulated to yield thermodynamic properties at any state within its realm of applicability.

5.6 Accuracy Estimates

In this section, accuracy estimates for selected thermodynamic properties calculated from the Gibbs free energy surface are discussed. The accuracy of a particular property depends on several factors including
Figure 6: LiBr/H₂O Enthalpy Isotherms and Isobars
Figure 7: LiBr/H₂O Entropy Isotherms and Isobars
the smoothness of the surface, the correlation of the available data and the accuracy of the data itself.

Irregularities in the Gibbs free energy surface (i.e. a lack of smoothness) can result from several factors. One such factor is overfitting of the data. The term overfitting describes a situation where the input data is well represented by the derived surface but there exist small scale irregularities or ripples in the surface. The irregularities are mathematical anomalies. Overfitting often results when there are too many adjustable constants included in the correlating equation.

Conversely, underfitting of the data can occur if too few adjustable constants are included in the correlating equation. Underfitting also can contribute to decreased accuracy of derived thermodynamic properties. Underfitting generally results in poor correlation of the data. The high correlation obtained in this study of all the available property data combined with the observed smooth curvature of the surface (see Figures 6 and 7) indicate that neither underfitting nor overfitting is a major factor in the derived correlation.

The question of the accuracy of the input data cannot be definitively answered from the analysis in
this study. However, the present study does provide a method of examining the thermodynamic consistency of the input data. Such analyses led to the weights assigned to the data in Section 4.6.

The accuracy estimates made here are based on comparisons between the best available data and the values derived from the Gibbs free energy surface. The estimates are included in Table 12 along with the independent variable ranges over which the estimates have been validated (i.e. the realm of applicability). Several aspects of these estimates require further discussion.

First, note that estimates have been made for all the properties considered in this study. Care must be exercised, however, if the Gibbs free energy expression derived in this study is used to calculate thermodynamic properties other than those considered here. Such calculations should be checked against experimental data when possible. Calculated properties involving higher order derivatives of the Gibbs free energy surface than considered in this study should be used with particular care.

Secondly, the heading "Realm of Applicability" in Table 12 refers to the ranges of the independent variables for which data are available for comparison.
Table 12: Accuracy Estimates of the Properties Derived from the Gibbs Free Energy Surface

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Accuracy</th>
<th>Realm of Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Heat</td>
<td>J/g·K</td>
<td>±0.16</td>
<td>0 → 130°C</td>
</tr>
<tr>
<td>Density</td>
<td>kg/m³</td>
<td>±3.0</td>
<td>0 → 100°C</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>%</td>
<td>±3.0</td>
<td>0 → 250°C</td>
</tr>
<tr>
<td>Activity Coefficient of LiBr</td>
<td>%</td>
<td>±3.0</td>
<td>Limited</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>J/g</td>
<td>±8.0</td>
<td>0 → 180°C</td>
</tr>
<tr>
<td>Entropy</td>
<td>J/g·K</td>
<td>±0.03</td>
<td>0 → 200°C</td>
</tr>
</tbody>
</table>

a: Magnitude scales for these properties are given in Tables 5, 6 and 11

b: Realms of applicability encompass saturated states (vapor/liquid) over the full composition range in each case. The temperatures, therefore, define the realms.

c: T = 25°C
p = 1.013 bar
0. < X < Crystallization
Care must be exercised when extrapolations beyond the ranges of the input data are attempted. For example, high temperature and high pressure extrapolations beyond the specified ranges are expected to yield questionable results. It should also be noted that most of the available data for LiBr/H₂O are saturated liquid data (vapor/liquid equilibrium). Thus the Gibbs free energy expression derived in this study has not been verified extensively at subcooled states. However, because of the weak effects of pressure on liquid properties, subcooled extrapolations are expected to yield accurate results over a limited pressure range.

Thirdly, note that two types of accuracy specifications are given in Table 12. These two are absolute and relative. Absolute specifications are given in the units of the property under consideration for specific heat, density, enthalpy and entropy. For these properties, the accuracy can be reasonably viewed as a constant over the entire realm of applicability. The vapor pressure and activity coefficient exhibit large ranges of magnitude and therefore accuracy specifications for these properties cannot be reasonably viewed as constant over the large ranges. Therefore relative specifications are given for these properties. The relative specifications are given as percentages of
the magnitude of the property under consideration (see entry under the heading "Units"). The observed discrepancies between the data and the Gibbs free energy surface derived values for these properties exhibit approximately constant percentage errors.

The overall success of the free energy surface method, applied to LiBr/H$_2$O, is evident from the accuracy estimates in Table 12. Values of the thermodynamic properties listed there can be readily calculated over the complete realm of applicability.

Particular note should be made of the excellent agreement obtained between the Gibbs free energy surface derived properties and the heretofore widely used data of McNeely. The agreement is demonstrated in Tables 6 and 11 and Figure 4.

5.7 Closure

The Gibbs free energy expression developed in this study provides a versatile tool for the analysis of absorption systems. The Gibbs free energy expression is intrinsically more useful and flexible in calculating thermodynamic properties of LiBr/H$_2$O than the tabular data compilations or limited property curve fits previously available. The expression provides accurate reproduction of all the available thermodynamic data on
LiBr/H₂O in the ranges of the independent variables of interest to absorption system designers. The widely used data of McNeely is only available over a portion of the ranges of interest of the independent variables. The Gibbs free energy expression of the present study not only accurately reproduces the McNeely data, but also the more recent experimental data at higher temperatures (such as [4,13]).

The flexibility of the Gibbs free energy expression provides other benefits. The expression can be readily integrated into absorption cycle computer models. Its use can eliminate multiple routines developed to predict individual thermodynamic properties. These features, combined with excellent accuracy of the derived properties, represent a significant extension of the modeling and design capabilities for LiBr/H₂O absorption systems. In the next chapter, a particular absorption system is studied thermodynamically using property values calculated from the Gibbs free energy surface developed.
Chapter 6

The Temperature Boosting Absorption Heat Pump Cycle

Utilizing LiBr/H2O

The present chapter provides a thermodynamic analysis of an existing absorption temperature boosting heat pump utilizing LiBr/H2O. The thermodynamic properties of LiBr/H2O needed in the analysis are generated from the Gibbs free energy surface developed in this study. The Gibbs free energy surface is discussed in Chapters 2 to 5.

In Section 6.1 a brief sketch of the development of the cycle is provided. In Section 6.2 the fundamentals of operation of the temperature booster are discussed. In Section 6.3 two performance parameters are discussed and a reversible analog to the temperature booster cycle is introduced. In Section 6.4 mass, energy and entropy balances are applied to an existing heat pump. In Section 6.5 the results are analyzed and a series of potentially efficiency enhancing design guidelines are discussed. Finally, in Section 6.6 conclusions are summarized.
6.1 History and Description

The absorption process has the potential to be utilized in a variety of cycle designs providing heating, cooling or energy storage. The literature pertaining to the absorption process includes a vast number of articles and books. A recent historical survey by Bjurstrom and Raldow [33] provides an excellent introduction to the technology. In that review, the authors cite several early references to the temperature booster cycle under the heading "The Reversed Absorption Process - Upgrading of Heat", e.g. [35,42,43]. These German and Russian language references indicate (English translations have not been found) that the cycle was known abroad by the 1950's. However, until recently very little work has been done on the temperature booster cycle in the United States.

The absorption temperature boosting heat pump operates by exchanging energy by heat transfer with other systems at 3 (or 4) different temperatures. The interactions between the cycle and its surroundings are shown schematically in Figure 8. Sources such as waste heat provide energy by heat transfer to the cycle at intermediate temperatures $T_G$ and $T_E$ and a portion of that energy becomes the output as heat transfer at a
Figure 8: Simplified Schematic of the Temperature Booster Cycle
higher temperature, $T_A$. The output occurs at the highest temperature in the cycle. The remainder of the input energy is typically discarded by heat transfer at the low temperature in the cycle, $T_C$.

The temperature booster cycle is applicable in many industrial plants where low temperature thermal energy sources, such as waste heat, are available and where the energy in a higher temperature stream can be utilized to conserve fuel. Thus the cycle can be thought of as a bottoming cycle which recovers a portion of the availability of a low grade waste heat stream. The cycle shows great promise as a means for improving the overall thermodynamic effectiveness and economics of certain industrial processes.

Several different temperature booster designs have been constructed and tested since 1975. Published cycle descriptions are available for the four research machines indicated in Table 13. The temperature boosters designed by Battelle Memorial Institute and Oak Ridge National Laboratory (ORNL) both employ LiBr/H$_2$O as the working fluid and, as a result, the two machines have many similarities. The machine designed by Rocket Research Co. requires teflon coated components due to the corrosive nature of sulfuric acid (H$_2$SO$_4$). Little is known about the machine designed by the Institute
Table 13: Existing Absorption Temperature Boosting Heat Pumps

<table>
<thead>
<tr>
<th>Research Laboratory</th>
<th>Working Fluids</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Battelle Memorial Institute</td>
<td>LiBr/H₂O</td>
<td>[18]</td>
</tr>
<tr>
<td>Oak Ridge National Laboratory</td>
<td>LiBr/H₂O</td>
<td>[21]</td>
</tr>
<tr>
<td>Rocket Research Co. Institute Français du Petrole</td>
<td>H₂SO₄/H₂O</td>
<td>[7]</td>
</tr>
<tr>
<td>Institute Français du Petrole</td>
<td>H₂O/NH₃</td>
<td>[8]</td>
</tr>
</tbody>
</table>

* - Fluid pairs specified in the order absorbent/refrigerant

Français du Petrole other than the fact that it uses H₂O/NH₃ as the working fluid.

The current investigation was motivated, in part, by the author's involvement with the Battelle Memorial Institute temperature booster. However, to avoid the use of proprietary information, the analyses in the present study are based on operating data from the ORNL machine which are in the open literature [21]. The ORNL machine was designed and constructed to demonstrate the feasibility and performance of the LiBr/H₂O temperature booster cycle. The published operating conditions are
summarized in the present chapter and form the basis of the analyses. The analyses and results are discussed in Sections 6.4 and 6.5.

6.2 Fundamentals of Operation

The discussion in the present section centers on the details of how the absorption temperature booster cycle operates. The discussion is designed to provide an understanding of the operation of the absorption temperature booster cycle without a detailed understanding of the absorption chiller cycle. However, for a more complete understanding of absorption technology it may be beneficial to compare the present discussion with a similar discussion of the absorption chiller cycle provided in [11]. The discussion here is separated into a general qualitative description of a LiBr/H₂O temperature booster, presented first, followed by a quantitative description of the ORNL machine.

6.2.1 Qualitative Description

The absorption temperature booster cycle produces a heat transfer as the output at a temperature higher than its input. Both the output temperature level and the output energy flow rate are key to the utilization of
the cycle for a particular application. The capability of the cycle to provide a heat transfer as the output at a temperature higher than the input heat transfers depends on the ability of the working fluids to store energy internally at one point in the cycle and release that stored energy at another point. Consider the working fluids LiBr/H$_2$O.

When a portion of the H$_2$O is boiled from the LiBr/H$_2$O solution, energy is stored in the solution. The energy is stored as a result of attractive intermolecular forces between LiBr and H$_2$O in the more concentrated solution. The stored energy is released when the H$_2$O returns to the solution by absorption. Thus the absorption of H$_2$O vapor into the liquid solution is an **exothermic process** (see Glossary). The energy released by the exothermic process increases the temperature of the solution as the vapor is absorbed.

The exothermic absorption process is the basis of the ability of the cycle to produce an output at a temperature higher than its input. Energy storage in one component and release in another component is an important feature of all absorption cycles. In absorption chiller cycles, the energy storage phenomenon is an undesirable feature which detracts from the desired performance. However, in the absorption
temperature booster cycle, energy storage is fundamental to operation of the cycle. Descriptions of the absorption temperature booster cycle components are presented next.

A schematic showing the major components of the LiBr/H₂O absorption temperature booster is provided as Figure 9. The components are labeled with standard absorption chiller terminology. The interactions between components take the form of fluid flows and the nature of these flows is indicated. Heat transfer interactions between the cycle and the system into which it is integrated are accomplished via water loops, labeled A, C, E and G.

The mass flows indicated on the schematic can be separated into two categories. The water loops form one category. These mass flows, involving water only, are external to the temperature booster cycle. The water loops interact with the cycle by heat transfer. The other category of mass flows are those that are internal to the cycle. These internal mass flows recirculate continuously during operation. In the following discussion, the use of the term water refers to the external heat transfer loops whereas H₂O is used to refer to water circulating within the cycle.

Since the working pair under consideration is
Figure 9: Absorption Temperature Boosting Heat Pump Schematic
LiBr/H₂O, the internal mass flows consist of LiBr/H₂O liquid and vapor streams. The vapor streams at 7 and 10 and the liquid streams between the condenser and the evaporator (8 and 9) are specified as pure H₂O following the discussion in Chapter 4 of the low volatility of LiBr. The mass and energy flow characteristics of each component are discussed next, beginning with the absorber.

The absorber is the component which delivers the output of the cycle. The output takes the form of heat transfer between the absorber and the corresponding water loop. The output energy is released when the H₂O vapor entering the absorber at 10 is absorbed into the concentrated LiBr/H₂O solution entering the absorber at 3. As mentioned previously, the absorption of H₂O vapor into the liquid solution is exothermic. The absorber heat transfer takes place at the highest temperature in the cycle. The combined mass flows exit the absorber as a homogeneous, diluted LiBr/H₂O solution.

As shown in Figure 9, the absorber receives concentrated solution from the generator (by way of the recuperative heat exchanger) at 3 and returns diluted solution to the generator at 4. From a mass flow perspective, the generator is simply an absorber operating in reverse. The generator (short for vapor
generator) receives a vapor/liquid two phase flow at 6 consisting of a dilute LiBr/H₂O solution and H₂O vapor and vaporizes a portion of the liquid phase by a heat transfer from the water loop. The energy input to the generator occurs at an intermediate temperature in the cycle. The generated vapor exits at 7 and the concentrated solution exits at 1.

The condenser and the evaporator have somewhat less complex mass flow characteristics. In the condenser, a quantity of H₂O enters at 7 in the vapor state and the entire quantity exits at 8 in the liquid state. Energy must be transferred to the condenser cooling water loop to achieve this phase change. The condenser heat transfer occurs at the low temperature in the cycle. The liquid leaving the condenser is pumped to the evaporator.

The evaporator reverses the phase change occurring in the condenser. The H₂O enters at 9 as liquid and exits at 10 as vapor by means of an input of energy by heat transfer from the evaporator water loop. The evaporator heat transfer occurs at an intermediate temperature in the cycle. The combined effect of the condenser, pump and evaporator is to change the state of the H₂O vapor from 7 to 10. The change of state typically involves a large increase in pressure and a
small temperature change. This method of compression exploits the substantial benefit in terms of the work required of pumping a liquid versus the alternative of using a vapor compressor. The result is a low requirement for work input to the cycle.

A change of phase also occurs in the expansion valve between 5 and 6. As the pressure of the liquid solution drops below its saturation pressure, a portion of the H$_2$O component undergoes a liquid-to-vapor phase change. The result is a two-phase flow entering the generator at 6.

The two pumps indicated on Figure 9 pump liquids between the components. The electrical energy required by these pumps is typically less than 1% of the energy input to the cycle as heat transfer in the generator and evaporator. Although this energy component is small enough to be neglected in subsequent discussions, it can be an important factor when the temperature booster cycle is evaluated economically.

In addition to the four main components in the cycle, the recuperative heat exchanger plays a key role in the cycle energy distribution. The liquid-to-liquid heat exchanger transfers energy between the two legs of the solution loop flowing between the generator and the absorber. On one side (from 2 to 3), the recuperative
heat exchanger provides the benefit of increased absorber temperatures for the same input temperature. On the other side (from 4 to 5) the effect is to increase the heat transfer requirements in the generator.

This completes the qualitative discussion of the cycle. A quantitative examination of the operating conditions in an actual cycle follows.

6.2.2 Quantitative Description

A tabulation of a nominal operating point of the ORNL temperature booster is provided as Table 14. Point numbers refer to Figure 9. These conditions represent a typical LiBr/H₂O absorption temperature booster. Included in the table are enthalpy and entropy values of LiBr/H₂O calculated from the Gibbs free energy surface generated as a part of the present study. Table 14 provides the information needed to understand the operating characteristics of the cycle.

The operating conditions within the cycle, provided in Table 14, are taken from measurements except as noted in the table. The existence of operating data tends to mask the dependent nature of many of the system variables. For an existing temperature booster, the independent variables are typically the temperatures and
Table 14: ORNL Temperature Booster Cycle State Points for the Nominal Operating Point

<table>
<thead>
<tr>
<th>Point</th>
<th>P (bar)</th>
<th>T (°C)</th>
<th>X_{LiBr}</th>
<th>h^e (J/g)</th>
<th>s^e (J/g-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0985</td>
<td>90.4</td>
<td>0.596</td>
<td>214.02</td>
<td>0.51926</td>
</tr>
<tr>
<td>2</td>
<td>0.626</td>
<td>90.4</td>
<td>0.596</td>
<td>214.05</td>
<td>0.51926</td>
</tr>
<tr>
<td>3</td>
<td>0.626</td>
<td>118.5</td>
<td>0.596</td>
<td>269.55</td>
<td>0.66629</td>
</tr>
<tr>
<td>4</td>
<td>0.626</td>
<td>127.2</td>
<td>0.550</td>
<td>278.31</td>
<td>0.76510</td>
</tr>
<tr>
<td>5</td>
<td>0.626</td>
<td>102.6</td>
<td>0.550</td>
<td>227.08</td>
<td>0.63301</td>
</tr>
<tr>
<td>6</td>
<td>0.0985</td>
<td>82.1</td>
<td>0.5594</td>
<td>227.08</td>
<td>0.63757</td>
</tr>
<tr>
<td>7</td>
<td>0.0985</td>
<td>84.5</td>
<td>0.0</td>
<td>2658.0</td>
<td>8.3744</td>
</tr>
<tr>
<td>8</td>
<td>0.0985</td>
<td>45.5</td>
<td>0.0</td>
<td>190.53</td>
<td>0.64527</td>
</tr>
<tr>
<td>9</td>
<td>0.626</td>
<td>45.5</td>
<td>0.0</td>
<td>190.57</td>
<td>0.64523</td>
</tr>
<tr>
<td>10</td>
<td>0.626</td>
<td>87.0</td>
<td>0.0</td>
<td>2655.0</td>
<td>7.5174</td>
</tr>
</tbody>
</table>

a - Since no property data is provided in [21], the pump exit states are calculated assuming isentropic flow, justified on the basis that the pump work requirements are considerably smaller than other energy flows in the system.

b - Pressure drops through the recuperative heat exchanger are ignored.

c - Calculated assuming a throttling process across the valve.

d - Composition of the liquid component of the two-phase flow.

e - Calculated using the Gibbs free energy expression developed in this study. See Chapter 5.
flow rates in the water loops. As these independent variables are changed the temperatures, pressures and compositions within the cycle dynamically adjust.

The water loop specifications for the ORNL nominal operating point are provided in Table 15. The specifications include the water temperatures, at the entrance and exit of each water loop, the water flow rates and the pressure drop from the inlet to the outlet. Carefully note that the inlet water temperatures to both the generator and the evaporator are essentially identical. This indicates that these components are being supplied in parallel from a common source. Alternative arrangements involving either a series supply or separate supplies to each component at different temperatures are also viable.

Finally, to complete the quantitative description of the cycle, the internal mass flow rates associated with the nominal operating point are provided in Table 15. The value for \( m_3 \) is taken from the ORNL measurements. The other internal mass flow rates are calculated from \( m_3 \), and the measured compositions listed in Table 14. The mass flow calculations are discussed in Section 6.4.2.

The operating conditions in the cycle are also shown in Figure 10. The figure displays the PTX
Table 15: ORNL Water Loop Specifications and Internal Mass Flow Rates for the Nominal Operating Point

<table>
<thead>
<tr>
<th>Water Loop</th>
<th>Water Temperatures(°C)</th>
<th>Flow (kg/min)</th>
<th>Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorber</td>
<td>98.79 134.10</td>
<td>26.95</td>
<td>0.207</td>
</tr>
<tr>
<td>Generator</td>
<td>98.92 89.69</td>
<td>113.31</td>
<td>0.017</td>
</tr>
<tr>
<td>Condenser</td>
<td>35.36 45.17</td>
<td>116.01</td>
<td>0.021</td>
</tr>
<tr>
<td>Evaporator</td>
<td>98.89 90.29</td>
<td>131.22</td>
<td>0.172</td>
</tr>
</tbody>
</table>

Internal Mass Flow Rates (kg/min)

\[ m_1 = m_2 = m_3 = 22.996 \]
\[ m_4 = m_5 = m_6 = 24.919 \]
\[ m_7 = m_8 = m_9 = m_{10} = 1.923 \]
Figure 10: PTX Diagram (Pressure-Temperature-Composition) of the Nominal ORNL Operating Point
(pressure-temperature-composition) characteristics of the ORNL nominal operating point. Curves representing constant composition, vapor/liquid saturation states are approximately straight lines when plotted in terms of the indicated coordinates \((\ln p, T)\). The line representing pure \(H_2O\) connects points \(6_v, 7, 8, 9\) and \(10\). Note that the numbered state points in Figure 10 correspond to the numbered cycle points in Figure 9.

Several features of Figure 10 require discussion. Note that the state points \(8, 6\) and \(1\) are all at the same pressure. The generator and condenser experience essentially the same pressure because the vapor path connecting the two components has a low flow resistance. Similarly, the absorber and the evaporator experience a common pressure shared by state points \(10, 4\) and \(3e\) in Figure 10.

Some of the state points in the cycle are subcooled liquid states: \(3, 5\) and \(9\). State \(6_v\) and \(7\) are superheated vapor states. Specification of these non-saturated state points requires three properties and therefore subcooled and superheated states cannot be represented accurately on a two-dimensional plot representing saturation states such as Figure 10. To enable the cycle to be drawn on Figure 10, subcooled states are represented by open circles placed so that
the temperature and composition coordinates are correct. Superheated states are represented by a circle with a superimposed plus sign. For the subcooled and superheated states the pressure coordinate does not apply.

As mentioned previously, the absorber operates at a temperature higher than the temperature of the heat inputs to the cycle which occur in the generator and the evaporator. The high temperature results from a release of energy by the exothermic absorption of the vapor. The energy is stored in the solution in the generator, and is released in the absorber. The increase in temperature in the absorber is represented in Figure 10 by a line connecting points 3 and 4. The highest temperature in the cycle occurs in the absorber and this high temperature is represented by the knee in the curve between 3 and 4. The solution exiting the absorber at 4 has been cooled by heat transfer to the absorber water loop.

The solution leaves the recuperative heat exchanger as a liquid at 5. It then passes through an expansion valve which controls the flow rate. As the solution flows through the expansion valve, a portion of the $\text{H}_2\text{O}$ component undergoes a liquid to vapor phase change in accordance with the properties of the solution. The
energy required for the vaporization is supplied by the internal energy of the flowing stream. Thus, the temperature of the stream drops as the composition of the liquid component becomes more concentrated. On entrance to the generator, the liquid component of the two phase flow is at the state marked \(6_1\) in Figure 10. The vapor component of the two phase flow, \(6_v\), is at the temperature and pressure of \(6_1\) but the composition of the vapor is essentially pure \(\text{H}_2\text{O}\). Note that in Table 14 state 6, representing the two phase flow, has been calculated assuming an adiabatic throttling process.

Thus, the mass flow entering the generator is a two phase flow with an overall composition identical to the composition at 5. The liquid phase is boiled in the generator, by heat transfer from the generator water loop, to generate \(\text{H}_2\text{O}\) vapor and concentrate the solution from the relatively dilute composition at point \(6_1\) to the more concentrated composition at point 1. The generated vapor mixes with the vapor entering the generator in the two phase flow. The combined vapor flows from the generator to the condenser.

The vapor entering the condenser at 7 is essentially pure \(\text{H}_2\text{O}\) in a superheated state. Thus the condenser must transfer an energy quantity from the
vapor, to reduce the temperature to the saturation temperature, in addition to the energy associated with the condensation. The $\text{H}_2\text{O}$ condensate formed leaves the condenser at 8 and is pumped to the evaporator at 9, which operates at a higher pressure.

The liquid delivered to the evaporator at 9 is subcooled relative to the evaporator operating pressure. Thus, vaporization of the $\text{H}_2\text{O}$ requires that the evaporator water loop supply an energy quantity to raise the liquid temperature to saturation in addition to the energy associated with the vaporization. The vapor leaves the evaporator at 10 and flows to the absorber.

The recuperative heat exchanger transfers energy by heat transfer between the two legs of the solution loop connecting the absorber and the generator. The liquid-to-liquid heat exchanger raises the temperature of the solution exiting the generator from 2 to 3. Simultaneously, the solution exiting the absorber is cooled from 4 to 5. The net result is significantly improved performance over the cycle operation without the recuperative heat exchanger as demonstrated by experiment in the ORNL study [21].

The point marked Be in Figure 10 is at a temperature higher than the maximum temperature attained in the absorber and is of interest because it helps to
predict the highest temperature in the absorber. The state 3e is $T=139\, ^\circ C$, $p=0.626\, \text{bar}$, $X_m=0.596$ mass fraction LiBr. This saturated state point is fixed by the composition of the solution entering the absorber and by the pressure in the absorber vapor space.

The temperature of 3e can be seen to represent an upper temperature bound in the absorber by the following reasoning. Note that the composition of the solution at states 3 and 3e are identical and also that the composition and the pressure define the maximum temperature at which the solution can exist (i.e. the saturation temperature). The solution entering the absorber at 3 is in a subcooled state. In the absorber, the solution is heated by the release of stored energy liberated as vapor is absorbed. Thus, as the solution temperature rises, the composition of the solution becomes more dilute (i.e. the $H_2O$ fraction increases). The fact that the composition of the solution at the point of highest temperature is more dilute than that at point 3e, implies that the temperature at point 3e represents an upper bound to the temperature rise in the absorber. Thus, the highest temperature in the absorber is between the temperatures of 3e and 4.
6.3 Temperature Booster Performance Measures

The output from the temperature booster cycle is a heat transfer at a temperature higher than the heat transfers which drive the cycle. Thus, a discussion of the performance of the cycle must include references to both the temperature of the output and the rate energy is delivered. For simplicity, the discussions in this section are based on the perspective that the temperature of the output is fixed and therefore the performance of the cycle is defined by the output energy rate.

The discussion in the present section is divided into four subsections. In Section 6.3.1 the rates at which energy and availability (see Glossary) are carried into the system by the water loops are calculated. In Section 6.3.2 performance measures based on energy and availability are defined and calculated. In Section 6.3.3 a model of an ideal absorption temperature booster cycle is developed. The performance measures for the ORNL machine are compared against identical measures for the ideal model. In Section 6.3.4 the effects of temperature on the performance measures is examined.
6.3.1 Water Loop Energy and Availability Calculations

The results of the calculations discussed in the present subsection are used in the following subsection to characterize the performance of the ORNL temperature booster. The net energy and availability carried into the control volume by the water flowing in each of the water loops are calculated based on the water loop data presented previously in Table 15.

Consider the four water loops on Figure 9. The net rate energy is carried from (+) or to (-) the corresponding components is given by

\[ \dot{m} \Delta h = \dot{m} c_p (T_e - T_i) \]  
(6.1)

where \( h \) is the specific enthalpy, \( \dot{m} \) denotes the mass flow rate, \( c_p \) is the isobaric specific heat of water, and \( T_i, T_e \) denote the temperature of the water entering and exiting the component, respectively.

The net rate availability is carried from (+) or to (-) a component by the associated water stream is

\[ \dot{m}(\Delta a_f) = \dot{m}(\Delta h - T_0 \Delta s) \]
\[ = \dot{m} c_p \left[ (T_e - T_i - T_0 \ln \left( \frac{T}{T_i} \right)) \right] \]  
(6.2)
where $a_F$ is the flow availability and $T_0$ is the temperature of the availability reference environment \([34]\). In writing Eqs. 6.1 and 6.2 the water in the loops has been regarded as incompressible and $c_p$ is assumed constant.

Using Eqs. 6.1 and 6.2 together with data from Table 15, the energy and availability rates for each of the four components have been evaluated and are listed in Table 17 on page 196. Note that about 52% of the energy carried into the cycle by the generator and evaporator water loops is carried away in the condenser cooling water stream. The accompanying availability transfer is relatively less significant (12% of the input) because the condenser cooling water temperatures depart only a few degrees from that of the availability reference environment, $T_0 = 300$ K (27 °C) and thus the energy carried by the water has a relatively low potential for use.

6.3.2 First and Second Law Performance Measures

A first law performance measure for the temperature booster cycle denoted by $\eta$, which may be called a coefficient of performance (COP), is defined here as the net rate energy is carried from the cycle by the absorber water loop divided by the sum of the magnitudes
of the net rates of energy transfer to the cycle from the generator and evaporator water loops. That is

\[ \eta = \frac{(m \Delta h)_{A}}{(-m \Delta h)_{G} + (-m \Delta h)_{E}} \]  

(6.3)

With values from Table 17, \( \eta = 0.44 \).

A second law performance measure for the temperature booster cycle denoted by \( \varepsilon \), which may be called an effectiveness, can be defined analogously. That is

\[ \varepsilon = \frac{(m \Delta a_{f})_{A}}{(-m \Delta a_{f})_{G} + (-m \Delta a_{f})_{E}} \]  

(6.4)

With values from Table 17, \( \varepsilon = 0.55 \).

No data on the pumps is provided in [211]. However, the pump work evaluated on the basis of isentropic flow for the pressures under present consideration is very small relative to the other energy flows in the system (on the order of 1 kJ/min). So, even with reasonable values of pump efficiency, the pump work can be ignored relative to the other energy and availability quantities involved in the temperature booster cycle. Furthermore, since the heat transfer from the pumps would be a
fraction of the pump work input, it follows that heat transfer from the pumps to the environment can be ignored as well. Accordingly, in writing Eqs. 6.3 and 6.4, and in subsequent discussions, the pump work is neglected. Also, heat transfer between the pumps and their surroundings is ignored.

6.3.3 Ideal Absorption Temperature Booster Cycle

To judge the potential for improvement in the thermodynamic performance of the temperature booster cycle, consider an ideal model based on the schematic in Figure 11. On this figure the heat transfers that drive and load the cycle occur at fixed temperatures. The direction of the heat transfers are indicated by the direction of the accompanying arrows. For the ideal model, no unavoidable heat transfers with the surroundings take place and the pump work is ignored. All processes within the dashed line defining the boundary are assumed to occur reversibly.

An energy rate balance on the system of Figure 11 reduces at steady-state to

\[ \dot{Q}_G + \dot{Q}_E = \dot{Q}_A + \dot{Q}_C \]  \hspace{1cm} (6.5)

For reversible operation at steady-state, the rate at
Figure 11: Ideal Absorption Temperature Booster Cycle
which entropy enters the system accompanying heat transfer equals the rate entropy exits accompanying heat transfer. That is,

\[ \frac{Q_G}{T_I} + \frac{Q_E}{T_I} = \frac{Q_A}{T_A} + \frac{Q_C}{T_C} \]  \hspace{1cm} (6.6)

In writing Eq. 6.6, it is assumed that \( T_G = T_E = T_I \) where \( T_I \) denotes the intermediate temperature of the system.

A first law performance measure for the ideal temperature booster cycle analogous to Eq. 6.3 is

\[ \eta^* = \frac{\dot{Q}_A}{\dot{Q}_G + \dot{Q}_E} \]  \hspace{1cm} (6.7)

Upon combination of Eqs. 6.5 to 6.7

\[ \eta^* = \frac{T_A T_I - T_C}{T_I T_A - T_C} \]  \hspace{1cm} (6.8)

A second law performance measure for the ideal temperature booster cycle analogous to Eq. 6.4 is

\[ \varepsilon^* = \frac{\dot{Q}_A (1 - T_0/T_A)}{\dot{Q}_G (1 - T_0/T_I) + \dot{Q}_E (1 - T_0/T_I)} \]  \hspace{1cm} (6.9)
The numerator of Eq. 6.9 is the rate of transfer of availability accompanying the heat transfer occurring at temperature $T_A$ [34]. Similar interpretations apply for the individual terms in the denominator. Upon rearrangement, Eq. 6.9 becomes

$$\varepsilon^* = \eta^* \frac{T_I - T_0}{T_A - T_0}$$

(6.10)

This form emphasizes the relationship between the energy and availability based performance measures. Alternatively, $\varepsilon^*$ can be written in terms of temperatures only as

$$\varepsilon^* = \frac{T_I - T_C}{T_I - T_0} \frac{T_A - T_0}{T_A - T_C}$$

(6.11)

Determination of values for $\eta^*$ and $\varepsilon^*$ requires that choices be made as to which cycle temperatures correspond to the temperatures $T_A$, $T_C$, and $T_I$ of Eqs. 6.8 and 6.11. The choices described next represent one reasonable alternative. With reference to Table 15, $T_A$ and $T_C$ are identified with the highest temperatures in the respective water loops: $T_A = 407$ K, $T_C = 318$ K. $T_I$ is identified with the average temperature in the generator and evaporator water loops: $T_I = 368$ K. Other choices may be made (such as identifying $T_I$ with the
high or low temperature in the generator or evaporator water loops) but those presented are believed to best complete the analogy between the reversible cycle and the actual temperature booster cycle. Based on these choices for the temperatures, Eq. 6.8 gives $\eta^* = 0.62$ and Eq. 6.11 gives $\varepsilon^* = 0.88$. When these are compared against the actual values calculated earlier: $\eta = 0.44$, $\varepsilon = 0.55$, it can be seen that the ORNL machine is performing at about 2/3 of its theoretical limit.

The differences between the values of the two performance measures calculated from actual operating data and the values of their counterparts for the ideal cycle suggest that some potential may exist for improving thermodynamic performance. This might be realized by lessening the effect of irreversibilities and losses. Section 6.4 is devoted to the quantitative evaluation of the irreversibilities and losses associated with the principal components of the cycle. In Section 6.5 design options for improving performance are surveyed. Before proceeding to Section 6.4, a brief discussion of the effects of temperature on cycle performance is provided.
6.3.4 Temperature Effects on Cycle Performance

An understanding of the effect of each of the temperatures on \( \eta \) and \( \varepsilon \) can be had by inference from their effect on \( \eta^* \) and \( \varepsilon^* \). The values of the partial derivatives of \( \eta^* \) and \( \varepsilon^* \) with respect to each of the temperatures is provided in Table 16. Note that the direction of the temperature effects on the performance measures, defined by the sign of the evaluated derivatives, is the same for both the energy and availability based coefficients. The values can be interpreted as follows. The positive values of the derivatives with respect to the heat input temperature, \( T_i \), indicate that the cycle performance will increase as the average temperature of heat addition to the cycle increases. The negative values for the derivatives with respect to \( T_A \) and \( T_C \) indicate that the cycle performance will increase as either the heat rejection temperature, \( T_C \), or the product temperature, \( T_A \), decreases.

In Appendix D, it is shown that the signs of the temperature derivatives of the performance measures are independent of the particular operating point chosen. Thus, the temperature effects discussed are representative of the temperature booster cycle at any operating point. These temperature effects are referred
Table 16: Temperature Effects on the First and Second Law Performance Measures of the Temperature Booster Cycle

<table>
<thead>
<tr>
<th>Derivative^a</th>
<th>Value (K^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{\partial \eta_{TB}}{\partial T_A} )</td>
<td>-0.005396</td>
</tr>
<tr>
<td>( \frac{\partial \eta_{TB}}{\partial T_I} )</td>
<td>+0.01079</td>
</tr>
<tr>
<td>( \frac{\partial \eta_{TB}}{\partial T_C} )</td>
<td>-0.005554</td>
</tr>
<tr>
<td>( \frac{\partial \varepsilon_{TB}}{\partial T_A} )</td>
<td>-0.001689</td>
</tr>
<tr>
<td>( \frac{\partial \varepsilon_{TB}}{\partial T_I} )</td>
<td>+0.004835</td>
</tr>
<tr>
<td>( \frac{\partial \varepsilon_{TB}}{\partial T_C} )</td>
<td>-0.007954</td>
</tr>
</tbody>
</table>

^a - Derivatives taken with all other temperatures held constant and evaluated at \( T_A = 407 \) K, \( T_I = 368 \) K, \( T_C = 318 \) K.
6.4 Thermodynamic Analysis of the Temperature Booster Components

The present section provides a detailed thermodynamic analysis of the ORNL temperature booster. The analysis includes mass balances, energy balances and entropy balances for steady-state operation. The analysis is based on the published ORNL operating data and the LiBr/H₂O property data derived in the present study. These data are summarized in Tables 13 and 14 of Section 6.3. The discussion begins with a review of the expected sources of irreversibility in the cycle.

6.4.1 Sources of Irreversibility and Availability Loss in the Temperature Booster Cycle

A discussion of the expected sources of irreversibility and availability loss in the temperature booster cycle is provided in the present subsection. The major sources of irreversibility are identified on the basis of physical reasoning guided by operating experience with an actual temperature booster cycle.

Heat transfer through finite temperature dif-
ferences is inherently irreversible. The predominant source of irreversibility in the temperature booster cycle is expected to be related to heat transfer since the major interactions between the cycle and its surroundings are heat transfers in the absorber, generator, evaporator and condenser. Significant heat transfer irreversibilities are expected in each of these components based on experience with similar systems. This source of irreversibility is also present in the recuperative heat exchanger. Fluid friction effects are coupled to the heat transfer effects due to the large density changes associated with vapor/liquid phase changes.

The flow of a fluid past a solid boundary is inherently irreversible due to viscous friction. Thus, the flows of LiBr/H$_2$O liquid and vapor within a temperature booster occur irreversibly. However, the fact that the work requirements for the liquid pumps are small suggests that liquid friction does not represent a major source of irreversibility in the cycle. The vapor flows are low density, low velocity flows and therefore frictional effects between the vapor and the solid boundaries is expected to contribute little to the total irreversibility of the cycle.

Unrestrained expansion, such as occurs at the
expansion valve, is another source of irreversibility in the cycle. The expansion process occurs between the highest and lowest pressures in the cycle. Since the expansion involves partial vaporization of the solution, a significant irreversibility can be expected in the flow through the expansion valve.

A secondary source of irreversibility in the cycle is the mixing of vapors at different temperatures. This irreversibility occurs in the generator as a result of two phenomena. One effect is that vapor enters the generator with the liquid solution and mixes with the vapor already present in the generator vapor space. The second effect is the fact that the temperature of the generated vapor depends on the saturation temperature of the solution. As the vapor evolves from solution, the saturation temperature changes. At the inlet to the generator, the relatively dilute solution boils at a lower temperature than the more concentrated solution at the exit end. Thus the vapors which evolve are at different temperatures. Some mixing occurs in the vapor space between the generator and condenser. This process is expected to contribute only a small fraction of the cycle irreversibility.

Another secondary source of irreversibility is associated with the absorption of vapor in the absorber.
In this device, the chemical potential of the $H_2O$ vapor is greater than the chemical potential of the $H_2O$ component of the LiBr/$H_2O$ solution flowing through the absorber. Thus, even though the vapor temperature is below the saturation temperature of the solution, the vapor is absorbed. This non-equilibrium absorption is irreversible.

In addition to the irreversibilities just mentioned, availability losses also take place. Losses occur due to unavoidable heat transfers from the component surfaces to the environment.

This concludes the discussion of the expected irreversibility sources and availability losses in the temperature booster cycle. In the next subsection, a detailed thermodynamic analysis of the absorber is presented which is aimed at quantifying the irreversibilities and losses in this component.

6.4.2 Absorber Analysis

Since the output from the temperature booster occurs at the absorber, the component analysis begins with the absorber. The analysis is based on the control volume defined by the dashed line in Figure 12. In addition to fluid flows across the control volume boundary, a heat transfer quantity, denoted $Q_{AL}$, is
Figure 12: Absorber Control Volume
shown. All heat transfer "losses" from the component to its operating environment (positive in the direction of the arrow) are lumped together in this term. The remainder of the labels in Figure 12 are identical to those in Figure 9 and are defined in Section 6.2.

Consider a mass balance on the absorber control volume.

Total Mass Balance:

\[ m_{Ai} + m_3 + m_{10} = m_4 + m_{Ae} \]  \hspace{1cm} (6.12)

But \( m_{Ai} = m_{Ae} \) so

\[ m_3 + m_{10} = m_4 \]  \hspace{1cm} (6.13)

LiBr Mass Balance:

\[ X_{m3} m_3 = X_{m4} m_4 \]  \hspace{1cm} (6.14)

Combining Eqs. 6.12 and 6.14 allows the vapor flow rate \( m_{10} \) to be calculated from the measured data as follows

\[ m_{10} = \frac{X_{m3}}{X_{m4}} - 1 \frac{m_3}{m_4} \]  \hspace{1cm} (6.15)
In the component analyses which follow, the mass flow rate values calculated from Eqs. 6.12 to 6.15 and appearing in Table 15 are used.

Consider an energy balance on the absorber control volume. The balance can be written as follows.

\[
\dot{Q}_{AL} = \dot{m}_{10}h_{10} + \dot{m}_{3}h_{3} - \dot{m}_{4}h_{4} + \dot{m}_{A}(h_{Ai} - h_{Ae})
\]  

Equation 6.16 has been arranged for calculation of the heat loss term denoted \(\dot{Q}_{AL}\). The numerical results of the absorber analysis as well as the results of the analyses of the other cycle components are provided in Table 17 on page 196.

Consider next an entropy rate balance for the absorber control volume. The object is to calculate the rate of entropy production \(\dot{\sigma}\) within the control volume. The entropy rate balance can be written as follows.

\[
\dot{\sigma}_{A} = \dot{m}_{4}s_{4} - \dot{m}_{3}s_{3} - \dot{m}_{10}s_{10} - \int_{s}^{\dot{Q}_{AL}} \frac{dT}{s} + \dot{m}_{A}(s_{Ai} - s_{Ae})
\]

The first three terms on the right side of Eq. 6.17 are composed of terms defined in Section 6.2. The last two terms require additional discussion.
The fourth term on the right side of Eq. 6.17 represents the entropy flowing from the absorber control volume with heat transfer to the environment. The integration is to be performed over the entire surface area of the control volume. In the present analysis, the integral is approximated by assuming that all heat transfer occurs at an average surface temperature taken as the temperature at state 10. That is

\[ \int_{\text{s}}^{\text{T}} \frac{dQ_{\text{AL}}}{T} = \frac{Q_{\text{AL}}}{T_{10}} \]  

(6.18)

The heat transfer, \( Q_{\text{AL}} \), is known from the energy balance in Eq. 6.16. The temperature \( T_{10} \), is the temperature of the vapor entering the absorber. Since \( T_{10} \) is the lowest temperature in the absorber, Eq. 6.18 overestimates the entropy flowing from the absorber to the environment. A simple calculation based on the upper temperature bound in the absorber (3e) indicates that the value obtained from Eq. 6.18 is within 15% of the actual value.

The last term in Eq. 6.17 represents the net entropy carried into the control volume by the water loop. The term is evaluated assuming the water flowing in the water loop to be incompressible. The entropy
difference between two states for an incompressible system is written as follows with reference to Eq. 1.38.

\[
\Delta s_{i-e} = \int_{i}^{e} \frac{c_p}{T} \, dt \quad (6.19)
\]

Assuming \( c_p \) is constant, Eq. 6.19 becomes

\[
\Delta s_{i-e} = c_p \int_{i}^{e} \frac{dT}{T} = c_p \ln\left(\frac{T}{T_i}\right) \quad (6.20)
\]

Eq. 6.20 is utilized for calculation of the entropy difference between the inlet and outlet of the water loops for each of the components.

6.4.3 Remaining Component Analyses

The energy and entropy analyses of the remaining components are similar to those discussed for the absorber. Therefore the equations are written next, along with the control volume definitions for each component.

For each of the components, the entropy equation includes a surface integral of the heat transfer divided by the temperature. The method used in this study for approximating these integrals is introduced in Section 6.4.2. For each of the components, except the recuperative heat exchanger, the integral is ap-
proximated by the heat transfer to the environment divided by the vapor temperature in the component. The heat transfer with the environment is calculated from the energy balance for each component. For the recuperative heat exchanger, the integral is approximated by the heat transfer with the environment divided by the average temperature on the shell side of the heat exchanger.

Detailed pressure measurements are not available in the ORNL report. Only the two vapor space pressure measurements are provided. Thus, as an approximation, the recuperative heat exchanger has been treated as if it has zero pressure drop. This assumption is footnoted in Table 14.

The values calculated for the heat transfer between the environment and the generator, condenser, evaporator and recuperative heat exchanger are, respectively, \( \dot{Q}_{GL} = 0.14 \text{ kJ/min}, \dot{Q}_{CL} = -17.5 \text{ kJ/min}, \dot{Q}_{EL} = -14.5 \text{ kJ/min}, \dot{Q}_{HL} = -0.37 \text{ kJ/min}. \) Negative values indicate heat transfer into the components from the environment whereas positive values indicate heat transfer from the components. Although no data on the environment temperature is available in [21], heat gains from the environment would be at odds with expectations based on typical environmental temperatures. Therefore
Energy Balance:

\[ \dot{Q}_{GL} = \dot{m}_6 h_6 - \dot{m}_1 h_1 - \dot{m}_7 h_7 + \dot{m}_G (h_{Gi} - h_{Ge}) \]  

(6.21)

Entropy Equation:

\[ \sigma_G = m_1 s_1 - m_6 s_6 + m_7 s_7 - \int \frac{d\dot{Q}_{GL}}{s} - m_G (s_{Gi} - s_{Ge}) \]  

(6.22)

Figure 13: Generator Control Volume
Energy Balance:

\[ \dot{Q}_{CL} = m_7 (h_7 - h_8) + m_C (h_{Ci} - h_{Ce}) \]  \hspace{1cm} (6.23)

Entropy Equation:

\[ \sigma_C = m_7 (s_8 - s_7) - \int_s^T \frac{dQ_{CL}}{T} - m_C (s_{Ci} - s_{Ce}) \]  \hspace{1cm} (6.24)

---

**Figure 14:** Condenser Control Volume
Energy Balance:

\[ \dot{Q}_{EL} = m_9(h_9 - h_{10}) + m_E(h_{Ei} - h_{Ee}) \] (6.25)

Entropy Equation:

\[ \sigma_E = m_9(s_{10} - s_9) - \int \dot{Q}_{EL} \frac{ds}{s} - m_E(s_{Ei} - s_{Ee}) \] (6.26)

Figure 15: Evaporator Control Volume
Energy Balance:

\[ \dot{Q}_{HL} = \dot{m}_2(h_2 - h_3) + \dot{m}_4(h_4 - h_5) \]  
(6.27)

Entropy Equation:

\[ \sigma_H = m_2(s_3 - s_2) + m_4(s_5 - s_4) - \int_{T}^{\infty} \frac{\dot{Q}_{HL}}{s} \]  
(6.28)

---

**Figure 16:** Recuperative Heat Exchanger Control Volume
Energy Balance:

\[ h_5 = h_6 \]  \hspace{1cm} (6.29)

Entropy Equation:

\[ \dot{\sigma}_T = m_5 (s_6 - s_5) \]  \hspace{1cm} (6.30)

---

**Figure 17:** Expansion Valve Control Volume
the validity of these numerical results, particularly those with negative signs, is doubtful. However, each of the foregoing heat transfer rates is less than 1% of the major energy transfer taking place in the respective components. Accordingly, because the magnitudes of these rates are relatively insignificant and some are anomalous, all are ignored in the subsequent discussions. Note that zero entries appear for them in Table 17 and for the accompanying availability transfers.

6.4.4 Summary of Numerical Results

The energy and entropy flows in each of the temperature booster components are represented by Eqs. 6.16, 6.17 and 6.21 to 6.30. A summary of the numerical results from these equations are provided in Table 17. The results are based on the measured operating data from the ORNL study [21] and thermodynamic property values generated from the Gibbs free energy surface for LiBr/H₂O derived as a part of this study along with the assumptions already discussed.

Note that each of the four major components transfers a similar magnitude of energy per unit time. The algebraic sum of these energy flow rates represents the net rate at which energy is being transferred into the cycle by the water loops.
Table 17: Summary of Energy and Availability Evaluations for the Components of the Temperature Booster Cycle

<table>
<thead>
<tr>
<th>Component</th>
<th>Energy (kJ/min)</th>
<th>Availability C (kJ/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q mAh</td>
<td>mAh f (1 - (\frac{T_0}{T})) Q</td>
</tr>
<tr>
<td>Abs</td>
<td>3984. 385.</td>
<td>914 64.</td>
</tr>
<tr>
<td>Gen</td>
<td>-4375. ~0</td>
<td>-803 ~0</td>
</tr>
<tr>
<td>Cond</td>
<td>4763. ~0</td>
<td>204 ~0</td>
</tr>
<tr>
<td>Evap</td>
<td>-4725. ~0</td>
<td>-870 ~0</td>
</tr>
<tr>
<td>Recup Hx</td>
<td>~0</td>
<td>~0 ~0</td>
</tr>
<tr>
<td>Exp Valve</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SUM</td>
<td>-353. 385.</td>
<td>-555 64.</td>
</tr>
</tbody>
</table>

a - Except for the irreversibility I, a positive sign denotes a net transfer from the corresponding component. A negative sign denotes a net transfer to the component.

b - The pumps are ignored in this evaluation as are unavoidable heat transfers from all components except the absorber.

c - The temperature of the availability reference environment, \(T_0\), is 300 K (27 °C).
The energy flow rates between the cycle and the environment, which are losses from the cycle, are calculated from the energy balances of Sections 6.4.2 and 6.4.3. The results are provided in Table 17 for each component. The only significant loss occurs in the absorber and represents approximately 10% of the water loop energy transfer. Large losses are expected in the absorber since this component has both the highest temperature and the largest surface area \([21]\) of any of the major components. In the other major components, the calculated losses represent less than 1% of the heat exchanger energy throughput in each case and have been set to zero because they are not significant. The availability losses with heat transfer to the environment, calculated using the same assumptions leading to Eq. 6.18, are also included in the table.

The sum of the heat transfer rates to the environment is also provided. Note that the magnitude of the net heat transfer rate to the environment compares well with the net heat transfer rate into the cycle from the water loops. This represents closure of the energy balance applied to the total cycle.

Values for the irreversibility in each component are also provided in Table 17. The irreversibility is calculated directly from the entropy production in each
component by multiplying by the availability reference environment temperature $T_0 = 300$ K. The table values indicate the relative significance of the irreversibilities occurring in each of the components. The largest irreversibility occurs in the absorber but the relative uniformity of distribution of irreversibility between the four major components suggests that the components are reasonably well matched.

An availability balance on the overall cycle was performed as a check on the component irreversibility calculations. Using the net rates of availability carried into the system by the water loops and the availability transfer rates with the environment from Table 17 results in a value of 491 kJ/min for the total cycle irreversibility. This compares well with the sum of the component irreversibilities given in Table 17 and represents closure of the availability balance applied to the total cycle.

Interpretation of the calculated irreversibilities is complicated by the fact that several irreversibility sources are contributing to the total in each component. The overall component analyses do not allow the contribution of each source to the total to be evaluated.
6.5 Proposed Modifications for Improved Performance

The present section provides a conclusion to the temperature booster cycle analysis work discussed in the preceding sections of Chapter 6. The discussion focuses on specific design modifications to the ORNL temperature booster directed at improving thermodynamic performance. The discussion of modifications is based on experience in operating the Battelle Memorial Institute absorption temperature booster as well as insight gained from the analyses conducted in the present study. Detailed design and economic analyses of the modifications have not been attempted. The discussion concerns only modifications involving standard engineering components. Several more technically challenging ideas involving components with characteristics beyond the current engineering state-of-the-art have been considered, but discarded as impractical on the basis of engineering judgment. Thus, economic considerations have entered the analysis implicitly.
6.5.1 Improvement of Existing Components

Two design recommendations that can improve the performance of a wide range of thermal systems are: (1) insulate the components to reduce unavoidable heat transfer to the environment and (2) increase the heat exchanger effectiveness of each heat exchanger in the system. These are considered next for the temperature booster.

Referring to Table 17, the rate of heat transfer from the absorber amounts to about 10% of the net energy carried from the component by the water loop. This loss can be reduced by better insulation of the outer surface of the absorber. Reduction of this loss would be expected to lead to better cycle performance in some combination of the following two ways: (1) the output temperature would be expected to rise and (2) the output energy rate would be expected to increase. If the entire absorber heat transfer loss could be redirected to the output (at the same output temperature) the COP would increase from 0.44 to 0.48. In an actual temperature booster the cycle states would be expected to adjust so that only a part of the energy savings would be available as output. Thus practical expectations of performance benefits from insulation are
more modest than the limiting case just described. The values of Table 17 suggest that the absorber is the only component that merits attention in this regard. The economic costs and benefits will govern the decision to insulate the absorber in future designs.

The option of improved heat exchanger performance must be approached with some caution. With the exception of the recuperative heat exchanger, the major components of the temperature booster are not simple heat exchangers. The components are mass and heat exchangers. Both of these phenomena must be considered in any design analysis. Either of the phenomenon can limit the overall performance of the component. This fact can be seen clearly by an examination of the standard designs of absorption components.

The standard design for a LiBr/H₂O generator is a pool boiler illustrated schematically in Figure 13. The water loop tubes are immersed in a slowly flowing pool of liquid solution. Vapor is boiled from the solution as heat transfer occurs. The design of a pool boiler generator is dominated by heat transfer considerations. Mass transfer considerations are secondary.

The standard absorber design, illustrated schematically in Figure 12, provides a significant contrast. Although the mass balance of the absorber looks like the
reverse of the generator, the design considerations of the two are totally different. The solution inlet to the absorber is a series of spray heads which direct the solution over the water tube bank. The tube bank is suspended in the vapor space above the liquid level in the absorber sump. Attention must be given to achieving adequate mass transfer characteristics as well as adequate heat transfer characteristics.

For example, if an absorber were designed to operate similarly to a pool boiler with a submerged bank of tubes, then insufficient vapor/liquid contact area would be available for mass transfer. The result would be decreased heat transfer to the absorber water loop even though the heat transfer characteristics of the device are more than adequate. Mass transfer can control the performance of the component.

The coupling between heat and mass transfer is critical in the design of the absorber and must be considered in the design of all the mass/heat transfer components. Overall system design requires balancing of the heat transfer and mass flow characteristics of all the components.

Consider the absorber and evaporator, both of which are connected by a low resistance vapor flow path in such a way that they experience essentially the same
pressure. The absorber and the evaporator are in vapor contact. Vapor is boiled off in the evaporator and absorbed into solution in the absorber at an identical rate. The average pressure in the vapor space and the vapor flow rate are determined by the heat transfer and mass flow characteristics of both components. For example, if several spray heads in the absorber were plugged, the average pressure in the vapor space would increase and the vapor flow rate would decrease due to the resulting reduction in vapor/liquid contact area. The evaporator conditions would also change dynamically to a new equilibrium point.

Similarly, a change in the evaporator water loop inlet temperature or flow rate would cause changes in the absorber operating point. Furthermore, any changes in either of these components would also effect the operating points in the generator and the condenser through flow rates, liquid compositions and temperatures.

This discussion of heat transfer and mass flow coupling throughout the cycle is provided to emphasize the difficulty of predicting the performance of a temperature booster. In particular, it is advisable to use caution in applying simple heat transfer design concepts to absorption system components which have mass
transfer requirements in addition to heat transfer requirements.

However, it is possible to account for coupled mass transfer by using a variation of standard heat transfer design concepts. The standard design concepts result in two complementary approaches to the improvement of the effectiveness of a heat exchanger. These are (1) the area approach and (2) the augmentation approach. The area approach involves simply increasing the heat transfer area whereas the augmentation approach involves geometry changes designed to increase the overall heat transfer coefficient. The mass transfer effectiveness of a mass exchanger can be viewed analogously to the heat transfer effectiveness. Improvements in mass transfer performance can be made by increased mass transfer area and by augmentation of mass transfer coefficients.

The performance of the ORNL temperature booster cycle could be significantly improved by reducing the temperature differences between the water loops and the cycle. The temperature differences could be readily reduced by improving the overall heat transfer and mass flow characteristics of the various components. This could be accomplished using existing component design by increasing the size of the components (i.e. increase
the heat and mass transfer areas). Alternatively, an augmentation approach involving novel component design may enable increased performance without an increase in component size.

The discussion in Section 6.3.4 of the temperature effects on cycle performance is useful in understanding the performance implications of the design modifications mentioned. However, from the design modification perspective, it is most useful to view the three temperatures which define the performance measures defined in Eqs. 6.8 and 6.11 in a different way than previously discussed. For the design modification analysis the internal cycle temperatures are identified with the three temperatures which define the performance measures. This alternative interpretation of the temperature effects on performance is useful for design modification analyses because these modifications tend to alter the internal cycle temperatures while the water loop temperatures are held constant.

The effect of the mass/heat exchanger design changes discussed in this subsection is to reduce the temperature differences between the water loops and the cycle by decreasing the mass and heat transfer resistances. Thus for fixed water loop temperatures and decreased mass and heat transfer resistances the cycle
temperatures are expected to change as follows. The average temperatures in the absorber and condenser are expected to decrease while the average temperatures in the generator and evaporator are expected to increase. Following from the analysis in Section 6.3.4, all of these changes will contribute to increased cycle performance.

An idea of the potential for improvement can be obtained from the results of the modeling done as a part of the ORNL study. A series of computer runs are reported with different values of the product $UA$ for each of the major components, where $U$ is the overall heat transfer coefficient and $A$ is the heat exchanger area. For these runs, the energy input and energy rejection temperatures were held constant and the product temperature was allowed to vary. Due to the varying output temperature, the interpretation of the resulting performance predictions is complicated.

One way to normalize the performance is to express the actual performance measure as a percentage of the corresponding ideal performance measure. By doubling the $UA$ product of each of the major system components (starting with the actual values), the ORNL model predicts that the COP expressed as a percentage of the ideal COP goes from 68.4% to 74.1%. Note that the ORNL
computer model predictions deviate slightly from the measured performance values which give a value of 71.3% for the ORNL nominal operating point. Thus with appreciably more effective heat exchangers, only slight increases are calculated for the cycle COP. Accordingly, although this option merits consideration, a dramatic improvement in cycle performance is not likely to result through the use of more effective heat exchangers. Ultimately, economic factors will govern the heat exchanger design decisions for future machines.

6.5.2 Potential For Recuperation

The potential for performance improvement based on existing components was discussed in Section 6.5.1. In the present subsection, the potential for performance improvement by recuperation is discussed.

An examination of the temperature booster operating conditions reveals several locations where energy transfers, within the cycle, appear to have potential for cycle performance improvement. The most promising option appears to be a potential to transfer energy from the high temperature solution stream at 5 to the low temperature $H_2O$ stream entering the evaporator at 9. This cycle modification would involve two additional liquid-to-liquid heat exchangers as shown in Figure 18.
Figure 18: Cycle Modifications
This modification would be expected to increase cycle performance by raising the average temperature of heat addition in the evaporator. This follows from the discussion of the temperature effects on performance in Section 6.3.

A rough idea of the magnitude of the potential performance improvement which might be expected from this cycle modification can be obtained by examining the energy flow rates involved. The energy rate required to raise the temperature of the liquid $\text{H}_2\text{O}$ at state 9 to the saturation temperature in the evaporator is 335 kJ/min. This represents less than 4% of the total energy input to the cycle. Thus, even if the design modification could deliver the majority of this energy to the absorber output loop with no additional energy costs, the potential performance improvement appears small.

Although additional recuperation opportunities do exist in the cycle, they do not appear to be practical possibilities. The slight performance improvements which are anticipated from modifications such as that shown in Figure 18 are expected to involve a significant additional economic cost. Thus recuperation opportunities beyond the primary recuperative heat exchanger are not expected to be significant.
6.6 Closure

In this chapter, detailed first and second law analyses of a LiBr/H₂O absorption temperature boosting heat pump are conducted on both an overall and a component-by-component basis. An ideal cycle is introduced which allows the best theoretical performance to be estimated for comparison purposes. Performance parameters based on energy and availability considerations are calculated using actual operating data and compared to values exhibited by the ideal cycle. Component analyses are performed utilizing versatile LiBr/H₂O thermodynamic property routines developed in this study.

The thermodynamic investigation reported upon in this chapter is believed to be the first in which the absorption temperature booster cycle components have been analysed comprehensively using both the first and second laws. The calculated component irreversibility values that are obtained provide insights beyond what is obtainable through energy analysis alone. The distribution of irreversibility serves as a guide to the designer. The relatively uniform distribution found in the ORNL temperature booster (Table 17) points to the conclusion that the components are reasonably well
selected and well matched. Accordingly, the design options for improved thermodynamic performance suggested on the basis of the thermodynamic evaluations conducted as well as practical operating experience with a temperature boosting heat pump cycle are expected to result in incremental gains only.
Chapter 7

Summary and Future Research

The first part of the present investigation involved the derivation of an analytic Gibbs free energy expression for LiBr/H₂O. The expression was derived by application of a multiproperty least squares criterion to a selected set of literature property data. The thermodynamic properties of LiBr/H₂O which can be readily calculated from the expression are particularly useful in the analysis of LiBr/H₂O absorption cycles. The accuracy and versatility of the Gibbs free energy expression make it a significant new tool for this type of analysis.

As an application of the Gibbs free energy expression, detailed first and second law analyses of a LiBr/H₂O absorption temperature boosting heat pump were conducted on both an overall and a component-by-component basis. The thermodynamic investigation conducted as a part of the present study is believed to be the first in which the absorption temperature booster cycle components have been analyzed comprehensively using both the first and second laws.
During the course of the present study, several specific opportunities have been identified for additional contributions in the area of absorption pair property correlation. Additional work on the system LiBr/H₂O might proceed along the following path. First, additional experimental data might be gathered, particularly in the temperature and pressure ranges extending above those of the currently available data. Secondly, it is anticipated that even better property correlation accuracy might be obtained by using variations on the functional form for the Gibbs free energy developed in the present study. Specifically, additional terms involving composition would be expected to improve the correlation of the activity coefficient data without negative consequences for the correlation of the other input data sets.

Several opportunities exist for documenting and extending the work of Schulz on the absorption pair H₂O/NH₃ [44] to make these results more useful to absorption system designers. Additional documentation of the comparison between the property predictions of the Schulz Gibbs free energy expression and the available data would establish the accuracy of the Schulz correlation. Furthermore, recalculation of the Schulz constants based only on data from [31] would be
expected to yield a more useful correlation for design purposes since these data are widely accepted.

In addition to the thermodynamic properties, transport properties for both LiBr/H₂O and H₂O/NH₃ are needed in absorption system design. Correlations of the transport properties viscosity and thermal conductivity as a function of temperature, pressure and composition would be particularly useful to designers.
Appendix A.

Gibbs Free Energy Surface and Property Expressions

This appendix provides a summary of the Gibbs free energy expression derived as a part of the present study. Values for the constants required to evaluate the expression are listed. Expressions for the thermodynamic properties considered in the present study are also provided. Additionally, a table of sample values of the various properties is provided as an aid to verification of independent calculations.

The dimensionless Gibbs free energy expression, given as Eq. 2.12, can be expressed in a more compact form as follows.

$$
\frac{X_1 \mu^o}{RT} + \frac{X_2 \mu^o}{RT} - 2\theta X_2 + 2\theta X_2 \ln m + \frac{4\theta X_1 A}{B} \ln(1 + Bm^{1/2}) + 2\theta X_2 Cm + \frac{4\theta X_2 D}{\alpha} \left[1 - (1 + \alpha m^{1/2}) \exp(-\alpha m^{1/2})\right] + \frac{2\theta X_2 E}{3} m^2
$$
The first term on the right side of Eq. A.1 represents the standard state properties of pure \( \text{H}_2\text{O} \). In the present study, the pure \( \text{H}_2\text{O} \) properties are calculated from the Steam Table equations of Keenan et al. [23]. The second term represents the standard state properties of \( \text{LiBr} \). The partial molar Gibbs free energy of \( \text{LiBr} \) in the standard state at the dimensionless temperature \( \theta \) and dimensionless pressure \( \pi \) can be written as follows (see the discussion of Eq. 2.29).

\[
\frac{\mu^o}{\mu^o_2} = \frac{\theta^o_{20^\circ}}{RT_s} - \frac{\theta^o_{20^\circ}}{RT_s} + \frac{L_1(\theta - \theta_0 - \theta \ln \theta_0)}{\theta_0} + \\
+ \frac{L_2[\theta_0(\theta - \theta_0) - \frac{\theta^o_0}{2}(\theta^2 - \theta_0^2)]}{\theta_0} + \\
+ \frac{L_3[-\frac{\theta^o_0}{2}(\theta - \theta_0) - \frac{\theta^o_0}{2}(\theta^3 - \theta_0^3)]}{\theta_0} + \\
+ K_1(\pi - \pi_0) + \frac{K_2}{2}(\pi^2 - \pi_0^2) + \\
+ K_3\theta(\pi - \pi_0) + K_4\theta^2(\pi - \pi_0)
\]  

(A.2)

The third and fourth terms of Eq. A.1 represent ideal solution properties for an electrolyte solution. These terms are discussed in detail in Section 1.3.2. The fifth term on the right side of Eq. A.1 results from
Pitzer's modified derivation of the Debye-Huckel electrolyte solution model (see Section 2.2). The parameter $A_{DH}$ is usually known as the Debye-Huckel constant. In the present study, this parameter depends on temperature and pressure as indicated in Eq. 2.2. A correlation published by Bradely and Pitzer [5] representing $A$ in terms of temperature and pressure is used to calculate values for $A_{DH}$. The remaining terms in Eq. A.1 are empirical terms, the composition dependence of which was suggested by Pitzer's analysis [39]. However, the temperature and pressure dependence of the last three terms, which is presented next, resulted from the present study.

The functional form employed for $C$, $D$ and $E$ can be written as follows

$$f_2(\theta,\pi) = F_1 \theta + F_2 + F_3 \theta + F_4 \theta^2 + F_5 \pi \theta + F_6 \pi +$$

$$+ F_7 \pi^2 + F_8 \pi \pi^2 + F_9 \pi^3 + F_{10} \pi^3$$

(A.3)

where $F_i, i=1,\ldots,10$ represent the constants $C_i$, $D_i$ and $E_i$. Evaluation of Eq. A.1 with Eqs. A.2 and A.3 is made possible by the parameter values provided in Table 18.

The following dimensionless thermodynamic property expressions, derived from Eq. A.1, are provided to
Table 15: Constant Values for Evaluation of the Gibbs Free Energy of LiBr/H₂O

---

Least Squares Result

<table>
<thead>
<tr>
<th>i</th>
<th>Cᵢ</th>
<th>Dᵢ</th>
<th>Eᵢ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.621729200695995E-1</td>
<td>-0.103064512543624E+2</td>
<td>0.72041542884317E-1</td>
</tr>
<tr>
<td>2</td>
<td>0.891080904954833</td>
<td>0.344399706798691E+1</td>
<td>-0.836230223094780E-1</td>
</tr>
<tr>
<td>3</td>
<td>-0.227800475946189</td>
<td>-0.396451605219227</td>
<td>0.207407543650433E-1</td>
</tr>
<tr>
<td>4</td>
<td>0.19435958160988E-1</td>
<td>0.374718762462649</td>
<td>-0.166478891547739E-2</td>
</tr>
<tr>
<td>5</td>
<td>0.132522430109248E-1</td>
<td>0.866873884267989</td>
<td>-0.795326885288716E-3</td>
</tr>
<tr>
<td>6</td>
<td>-0.228241399727267E-1</td>
<td>0.444311152956288</td>
<td>0.464233140604620E-4</td>
</tr>
<tr>
<td>7</td>
<td>-0.126107857312263E-5</td>
<td>0.140830353209046E-1</td>
<td>-0.967113570349287E-4</td>
</tr>
<tr>
<td>8</td>
<td>-0.934063448237055E-2</td>
<td>0.554164386035154</td>
<td>0.57945750016439E-3</td>
</tr>
<tr>
<td>9</td>
<td>0.162442517944328E-2</td>
<td>0.886087436722391E-1</td>
<td>-0.10392493757549E-3</td>
</tr>
<tr>
<td>10</td>
<td>0.59045262617817E-2</td>
<td>-0.173156216469010</td>
<td>-0.18590405874707E-3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>i</th>
<th>Lᵢ</th>
<th>Kᵢ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.198431513667500E+3</td>
<td>-0.120513288344227E+1</td>
</tr>
<tr>
<td>2</td>
<td>0.115866159260454E+3</td>
<td>0.635531036192333</td>
</tr>
<tr>
<td>3</td>
<td>-0.16777510683728E+2</td>
<td>0.809178760916438</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>-0.13324435965644</td>
</tr>
</tbody>
</table>

Related Constants

| h₂₀ °/RTₛ | 75.842 | pₛ     | 10. bar |
| s₂₀ °/RTₛ | 58.17105 | α      | 2.     |
| θₒ       | 1.0    | B      | 1.2    |
| Tₒ       | 1.0    | Mₗ     | 86.845 |
| R         | 8.3144J/mole-K | Mₘ     | 18.015 |
| Tₛ       | 100.0 K |        |        |
assist future application of the gibbs free energy expression for LiBr/H₂O.

Specific Heat:

\[
\frac{-X_1}{\theta} a^2 \mu_1^o \frac{\partial^2}{\partial \theta^2} \frac{-X_2}{\theta} a^2 \mu_2^o \frac{\partial^2}{\partial \theta^2} + \frac{RT_s}{\theta} \frac{\partial}{\partial \theta} \frac{RT_s}{\theta} \frac{\partial}{\partial \theta} + \frac{4X_1}{\theta} \frac{\partial A_{DH}}{\partial \theta} \frac{\partial^2}{\partial \theta^2} + \frac{4X_2}{\theta} \frac{\partial A_{DH}}{\partial \theta} \frac{\partial^2}{\partial \theta^2}
\]

\[
+ \frac{-2}{\theta}[\frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial \theta^2}] \ln(1 + Bm^{1/2}) + \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} + \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} \frac{2X_1}{\theta} e^{m^2} \frac{\partial E}{\partial \theta} \frac{\partial^2}{\partial \theta^2} + \frac{2X_2}{\theta} e^{m^2} \frac{\partial E}{\partial \theta} \frac{\partial^2}{\partial \theta^2} + \frac{-2}{\theta}[\frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial \theta^2}](1 - (1 + \alpha m^{1/2}) \exp(-\alpha m^{1/2}))
\]

Specific Volume:

\[
\frac{\nu_R}{\frac{X_1}{\theta} \frac{\partial \mu_1^o}{\partial \theta} \frac{\partial^2}{\partial \theta^2} + \frac{X_2}{\theta} \frac{\partial \mu_2^o}{\partial \theta} \frac{\partial^2}{\partial \theta^2} + \frac{4X_1}{\theta} \frac{\partial A_{DH}}{\partial \theta} \frac{\partial^2}{\partial \theta^2} \ln(1 + Bm^{1/2}) + \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} \frac{2X_1}{\theta} e^{m^2} \frac{\partial E}{\partial \theta} \frac{\partial^2}{\partial \theta^2} + \frac{2X_2}{\theta} e^{m^2} \frac{\partial E}{\partial \theta} \frac{\partial^2}{\partial \theta^2} + \frac{-2}{\theta}[\frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial \theta^2}](1 - (1 + \alpha m^{1/2}) \exp(-\alpha m^{1/2}))
\]

\[
+ \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} \frac{2X_1}{\theta} e^{m^2} \frac{\partial E}{\partial \theta} \frac{\partial^2}{\partial \theta^2} + \frac{2X_2}{\theta} e^{m^2} \frac{\partial E}{\partial \theta} \frac{\partial^2}{\partial \theta^2} + \frac{-2}{\theta}[\frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial \theta^2}](1 - (1 + \alpha m^{1/2}) \exp(-\alpha m^{1/2}))
\]

\[
+ \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} \frac{2X_1}{\theta} e^{m^2} \frac{\partial E}{\partial \theta} \frac{\partial^2}{\partial \theta^2} + \frac{2X_2}{\theta} e^{m^2} \frac{\partial E}{\partial \theta} \frac{\partial^2}{\partial \theta^2} + \frac{-2}{\theta}[\frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial \theta^2}](1 - (1 + \alpha m^{1/2}) \exp(-\alpha m^{1/2}))
\]
Chemical Potential of $H_2O$:

$$
\mu_{1R} = \frac{\mu_1^0}{RT_s} + 2\lambda\theta(\ln(1+Bm^{1/2}) - \frac{2}{2}) + \frac{A_{DH}m^{3/2}}{1+Bm^{1/2}} + \frac{Cm^2}{1+Bm^{1/2}}
- Dm^2\exp(-\alpha m^{1/2}) - \frac{2}{3} E_m
$$

Mean Activity Coefficient of LiBr:

$$
\ln \gamma_{\pm} = -A_{DH}\{\frac{1}{2} - \ln(1+Bm^{1/2})\} + 2Cm + \frac{2D}{\alpha^2} \{1 - (1+\alpha m^{1/2}) - \frac{2}{\alpha} \exp(-\alpha m^{1/2})\} + \frac{E_m}{2}
$$

Enthalpy:

$$
\Delta h_R = \frac{X_1}{RT_s} \left[ \mu_1^0 - \frac{\partial \mu_1^0}{\partial \theta} \right] + \frac{X_2}{RT_s} \left[ \mu_2^0 - \frac{\partial \mu_2^0}{\partial \theta} \right] + \frac{4X_1 \theta^2}{\alpha} \frac{\partial A_{DH}}{\partial \theta} + \frac{\ln(1+Bm^{1/2})}{\alpha^2} - \frac{2X_2m\theta^2}{\alpha} - \frac{4X_1 \theta^2}{\alpha} \frac{\partial D}{\partial \theta} - \frac{2}{\alpha} \exp(-\alpha m^{1/2}) + \frac{3X_1 \theta^2}{\alpha} \frac{\partial E}{\partial \theta}
$$

(A.6) (A.7) (A.8)
Entropy:

\[
\begin{align*}
S_R &= \frac{-X_1 \theta \mu_1^o}{RT_5 \theta} - \frac{X_2 \theta \mu_2^o}{RT_5 \theta} - 2X_2 (\ln m - 1) + \\
& \quad + \frac{4X_2}{B} \left( A_{DH} + \theta \frac{\partial A_{DH}}{\partial \theta} \right) \ln(1 + Bm^{1/2}) + \\
& \quad + \frac{4X_2}{\theta} \left( C + \frac{2X_2 m^2}{\theta} \right) \frac{\partial E}{\partial \theta} - 2X_2 m (C + \theta \frac{\partial C}{\partial \theta}) - \frac{2}{3} (E + \theta \frac{\partial E}{\partial \theta}) + \\
& \quad - \frac{4X_2}{\alpha} \left( \frac{\partial D}{\partial \theta} \right) (1 - (1 + \alpha m^{1/2}) \exp(-\alpha m^{1/2})) \frac{\partial D}{\partial \theta}.
\end{align*}
\]

(A.9)

A table of sample values calculated from Eqs. A.4 to A.9 is provided as Table 19. These values will aid the independent verification of the calculated properties.
<table>
<thead>
<tr>
<th>Property</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>$c_p^{R}$</td>
<td>8.35128043758712</td>
</tr>
<tr>
<td>$v_R$</td>
<td>$2.22140035841824E-2$</td>
</tr>
<tr>
<td>$h_R$</td>
<td>1.47136989768626</td>
</tr>
<tr>
<td>$s_R$</td>
<td>0.836394632927439</td>
</tr>
<tr>
<td>$Y^*$</td>
<td>1.31978139618064</td>
</tr>
</tbody>
</table>

States (each state is a vapor/liquid equilibrium state)
1 : $\theta=2.9815$, $\pi=0.00269805$, $X=0.2$ mass fraction LiBr
2 : $\theta=2.9815$, $\pi=0.0007931$, $X=0.5$ mass fraction LiBr
3 : $\theta=3.7315$, $\pi=0.033586$, $X=0.5$ mass fraction LiBr
Appendix B.

Temperature and Pressure Dependence of C, D and E in Eq. 2.12

Three candidate functional forms for the temperature and pressure dependence of C, D and E in Eq. 2.12 were introduced in Eqs. 2.13 to 2.18. The first of these three was chosen because it has been used successfully in a similar application [44]. The remaining two functional forms were developed by a systematic reasoning procedure, similar to that used by Fortier and Desnoyers [14], based on two different sets of assumptions. Although the reasoning procedure detailed in this Appendix is not based on deductions from first principles, some insight into the mathematical structure of the resulting expression is provided by the reasoning used. Note that one of the important features of each of the functional forms considered is linearity in the respective constants. The advantages of this feature are discussed in Chapter 3.
This section presents a detailed development of the reasoning leading to Eq. 2.17. Following Fortier and Desnoyers, the first step is to assume a specific functional form for derivatives of the terms involving C, D and E in Eq. 2.12. Then, two integrations lead to the functional form for C, D and E presented earlier as Eq. 2.17. The assumptions made in this development are justified ultimately by the ability of the resulting functional form to reproduce the experimental data. However, prior to the implementation of the least squares computations, the development of the functional form was guided primarily by the goals of simplicity and tractability.

For simplicity, the current development centers on only one of the empirical terms in Eq. 2.12. However the reasoning applies equally well to any of the empirical terms. Consider the term involving C.

\[ g_{RC} = 20X_2C(\theta,\nu)m \]  
(B.1)

The subscript R denotes the dimensionless specific Gibbs free energy and subscript C denotes the term involving C. Some simplicity of interpretation is gained later in the development if the composition dependence and the
constant are factored out at this point. The quantity \( g_{RCX} \) is defined as follows.

\[
g_{RCX} = \frac{g_{RC}}{2X_2m} = \theta C(\theta, \pi) \quad (B.2)
\]

The premise of the reasoning procedure is the assumption of a functional form for derivatives of the empirical terms of the Gibbs free energy. The following development is based on the assumed functional forms for the derivatives listed next.

\[
\frac{\partial^2 g_{RCX}}{\partial \theta^2} \pi = a_1 + a_2 \theta + a_3 \pi \quad (B.3)
\]

\[
\frac{\partial^2 g_{RCX}}{\partial \theta \partial \pi} = b_1 + b_2 \theta + b_3 \pi \quad (B.4)
\]

\[
\frac{\partial^2 g_{RCX}}{\partial \pi^2} \theta = e_1 + e_2 \theta + e_3 \pi \quad (B.5)
\]

Where the \( a \)'s, \( b \)'s and \( e \)'s are constants. Upon integration these simple linear forms for the 2nd derivative terms yield a functional form for \( C \).

Indefinite integration of Eq. B.3 gives

\[
\frac{\partial g_{RCX}}{\partial \theta} \pi = a_1 \theta + \frac{a_2 \theta^2}{2} + a_3 \pi \theta + I_1(\pi) \quad (B.6)
\]
where \( I_1(\pi) \) is an integration function which may depend on \( \pi \). Integrating Eq. B.6 gives

\[
g_{RCX} = \frac{a_1}{2} \pi^2 + \frac{a_2}{6} \pi^3 + \frac{a_3}{2} \pi^2 + I_1(\pi)\theta + I_2(\pi) \quad (B.7)
\]

Once again, \( I_2(\pi) \) must be introduced as an integration function to maintain generality. Next, a similar result is obtained from Eq. B.4. Depending on the order in which the integrations proceed, Eq. B.4 can be solved for \( g_{RCX} \) as follows.

\[
g_{RCX} = b_1 \pi^2 + \frac{b_2}{2} \pi^3 + \frac{b_3}{3} \pi^2 + \int I_3(\theta)d\theta + I_4(\pi) \quad (B.8)
\]

Or,

\[
g_{RCX} = b_1 \pi^2 + \frac{b_2}{2} \pi^3 + \frac{b_3}{3} \pi^2 + \int I_5(\pi)d\pi + I_6(\theta) \quad (B.9)
\]

And Eq. B.5 can be integrated twice to yield

\[
g_{RCX} = \frac{e_1}{2} \pi^2 + \frac{e_2}{2} \pi^3 + \frac{e_3}{6} \pi^3 + I_7(\theta)\pi + I_8(\theta) \quad (B.10)
\]

Next, assume for simplicity that the integration functions can be adequately approximated by quadratic polynomials in their respective independent variables. That is, assume
\[ I_n(\xi) = y_{n1} + y_{n2}\xi + y_{n3}\xi^2 \quad (B.11) \]

where the \( y \)'s are constants and \( \xi \) represents either \( \theta \) or \( \pi \) depending on the value of \( n \).

Upon combination of Eq. B.11 with Eqs. B.7 to B.10, four expressions for \( g_{RCX} \) are obtained. Each of these expressions embodies one of the assumed functional forms in Eqs. B.3 to B.5. The goal of obtaining a single expression which embodies all three of the assumed functional forms can be achieved simply by adding the four expressions for \( g_{RCX} \) together. After collecting terms, the following result is obtained.

\[ g_{RCX} = C_1 + C_2\theta + C_3\theta^2 + C_4\theta^3 + C_5\pi^2 + C_6\pi^3 + C_7\pi^2\theta + C_8\pi + C_9\pi^2 + C_{10}\pi^3 \quad (B.12) \]

The \( C \)'s in Eq. B.12 are constants related to the \( a \)'s, \( b \)'s and \( e \)'s. The functional form for \( C(\theta,\pi) \) given as Eq. 2.17 is obtained by dividing Eq. B.12 by \( \theta \). This follows from the definition of \( g_{RCX} \) in Eq. B.2.

A parallel reasoning procedure for the temperature and pressure dependence of \( D \) and \( E \) lead to functional forms identical to Eq. 2.17. Thus, the origin of Eq. 2.17 as the functional form for each of \( C, D \) and \( E \) is shown.
B.2 Candidate Function Number 3

This section presents a detailed development of the functional form selection process leading to Eq. 2.18. This development closely parallels the development in the preceding section. In the preceding development, the function C was obtained by assuming functional forms for the 2nd derivatives of $g_{RCX}$ (defined in Eq. B.2) with respect to temperature and pressure. The present development presents a variation of the procedure.

For simplicity, consider only the term in Eq. 2.12 involving C. This term was written previously as

$$g_{RC} = 2B x_2 C(\theta, \pi) m$$

As in the previous development, the composition dependence and the constant factor are divided through to give

$$g_{RCX} = \frac{-g_{RC}}{2X_2^m} = C(\theta, \pi)$$

(B.2)

At this point, there is a departure from the previous development. In the present development, simple functional forms are assumed for derivatives of the empirical terms divided by the temperature. Furthermore, the derivatives of interest are chosen to be the second derivatives with respect to inverse temperature
and the pressure. This choice is one of many possible ways to implement the method of Fortier and Desnoyers [14]. The details of the procedure follow.

The dependent variable is chosen to be the Gibbs free energy divided by the temperature. Focusing attention on the empirical term involving \( C \), the following result is obtained by dividing Eq. B.2 by \( \theta \).

\[
C(\theta, \pi) = \frac{g_{RCX}}{\theta}
\]  

(B.13)

Thus the present development proceeds directly in terms of \( C \).

The following functional forms for derivatives of \( C \) with respect to inverse temperature and pressure are assumed

\[
\frac{\partial^2 C}{\partial (1/\theta)^2} = a_1 + \frac{a_2}{\theta} + a_3 \pi
\]  

(B.14)

\[
\frac{\partial^2 C}{\partial (1/\theta) \partial \pi} = b_1 + \frac{b_2}{\theta} + b_3 \pi
\]  

(B.15)

\[
\frac{\partial^2 C}{\partial \pi^2} = e_1 + \frac{e_2}{\theta} + e_3 \pi
\]  

(B.16)

where the \( a \)'s, \( b \)'s and \( e \)'s are constants. Note that the functions are linear in the constants. These linear
functions are integrated next to obtain a functional form for $C$.

Indefinite integration of Eq. B.14 gives

$$\frac{\Delta C}{\delta(l/\theta)} = a_1 \frac{1}{\theta} + a_2 \frac{1}{2 \theta^2} + a_3 \frac{\pi}{\theta} + I_1(\pi)$$  \hspace{1cm} (B.17)

where $I_1(\pi)$ is an integration function which may depend on $\pi$. Integrating Eq. B.17 indefinitely gives

$$C = \frac{a_1}{2 \theta^2} + \frac{a_2}{6 \theta^3} + \frac{a_3}{2 \theta^2} + \frac{\pi}{\theta} + I_1(\pi) + I_2(\pi)$$  \hspace{1cm} (B.18)

where $I_2(\pi)$ is introduced as an integration function to maintain generality. Next, a similar result is obtained from Eq. B.15.

Depending on the order of integration, the solution of Eq. B.15 for $C$ takes one of the following two forms.

$$C = \frac{b_1 \pi}{\theta} + \frac{b_2 \pi^2}{2 \theta} + \frac{b_3 \pi^2}{2 \theta} + \int I_3(1/\theta)d(1/\theta) + I_4(\pi)$$  \hspace{1cm} (B.19)

Or,

$$C = \frac{b_1 \pi}{\theta} + \frac{b_2 \pi^2}{2 \theta} + \frac{b_3 \pi^2}{2 \theta} + \int I_5(\pi)d\pi + I_6(1/\theta)$$  \hspace{1cm} (B.20)

Also, Eq. B.16 can be integrated with the following result.
As in the preceding development, the next step is to assume that the integration functions can be represented by quadratic polynomials in their respective independent variables. That is,

\[ I_n(\zeta) = y_{n1} + y_{n2}\zeta + y_{n3}\zeta^2 \] (B.11)

where the \( y \)'s are constants and \( \zeta \) represents either \( 1/\theta \) or \( \pi \).

Substitution of Eq. B.11 into each of Eqs. B.18 to B.21 results in four different expressions for \( C \). Each of these four embodies one of the assumed functional forms in Eqs. B.14 to B.16. Summing these four functional forms into a single expression and collecting terms results in the functional form presented previously as Eq. 2.18. This summation ensures that each of Eqs. B.14 to B.16 is embodied in the final expression. A parallel reasoning procedure for the temperature and pressure dependence of \( D \) and \( E \) results in functional forms identical to Eq. 2.18.
Appendix C.

Glossary

**Absorbent** - in the present study, absorption pairs are specified in the order absorbent/refrigerant. The role of the absorbent is to transport the refrigerant between the absorber and the generator. In the case of a LiBr/H$_2$O temperature booster, the absorbent (LiBr) absorbs the H$_2$O vapor in the absorber and transports it to the generator in liquid form. In the generator the absorbent is again concentrated by boiling off the refrigerant (H$_2$O). See the refrigerant entry in this appendix.

**Availability** - a thermodynamic property of a system which reflects the maximum possible work obtainable as the system is brought into equilibrium with an availability reference environment. In this study, availability refers to the thermomechanical availability as defined in [34].

**Component Pressure of Component i** - the product of the mole fraction of component i and the system.
pressure. For ideal gas mixtures, this quantity is identical to the partial pressure.

**Ideal Solution** - a hypothetical model solution which exhibits thermodynamic properties representative of a class of real solutions. Two different ideal solutions are introduced in Sections 1.3.2 and 1.3.3. The relationship between these two is examined in detail in [46].

**Electrolyte** - an electrolyte is a substance that dissociates into ions when dissolved in certain solvents (known as ionizing solvents). Strong electrolyte solutions are those in which most of the electrolyte is dissociated. Weak electrolyte solutions exhibit a lesser degree of dissociation. The combination of LiBr and H2O (liquid) produces a strong electrolyte solution in which the Li and Br ions are essentially completely dissociated. The long range nature of the electrostatic forces between ions is the factor that causes the unique characteristics that electrolyte solutions exhibit.

**Excess Function** - a function which represents the difference between a thermodynamic property and a corresponding model. The excess Gibbs free energy is introduced in Eqs. 1.76 and 1.91.
**Exothermic Process** - a chemical process such as a chemical reaction or a mixing of two components with the following characteristic. When the process takes place adiabatically in a closed system, the temperature of the system after the process is greater than before the process. The temperature rise is caused by the liberation of chemical internal energy. Examples include combustion and mixing of certain components such as LiBr and H$_2$O.

**Extensive property** - a thermodynamic property, the value of which is proportional to the mass of the system under consideration. Examples: volume, enthalpy and Gibbs free energy. An extensive property is additive in the sense that its value for the whole system is the sum of the values for its parts.

**Intensive property** - a thermodynamic property that is independent of the size or extent of the system under consideration. Examples: temperature, pressure and specific volume.

**Mole Fraction of Component i** - a measure of composition equal to the number of moles of component $i$ divided by the total number of moles.

**Phase Equilibrium** - the subject of phase equilibrium
deals with the thermodynamic conditions necessary for two or more phases of matter to coexist at equilibrium.

**Refrigerant** - in the present study, absorption pairs are specified in the order absorbent/refrigerant. The term refrigerant derives from the use of absorption cycles as refrigeration cycles. In the case of a LiBr/H₂O temperature booster, the refrigerant (H₂O) recirculates continuously through each of the components in the cycle.

**Solution** - a single phase of matter containing more than one component. A solution may be gas, liquid or solid. The properties of a solution are dependent on the temperature, pressure and the amount of the individual components. In general, solutions exhibit solubility limits, which are regions of the independent variable space where the components are not mutually soluble.

**Working Pair** - a binary component solution used in absorption chillers and heat pumps. Examples: H₂O/NH₃ and LiBr/H₂O.
Appendix D.

Temperature Dependence of the Temperature Booster Performance

An idea of the temperature dependence of the absorption temperature booster cycle performance can be obtained by inference from the characteristics of the ideal model. This point is discussed in Section 6.3.4 where numerical values for the derivatives of the performance measures with respect to temperature are presented. In the present appendix, the derivatives are written in terms of the temperatures and it is shown that the direction of the influence of each of the temperatures on the cycle performance (i.e. the sign of the derivative) is independent of the operating point.

D.1 Coefficient of Performance (COP)

The COP of the ideal temperature booster cycle is given in Eq. 6.8 in terms of the three temperatures in Figure 8. Equation 6.8 is rewritten here for convenience.
\[ \eta^* = \frac{T_A T_I - T_C}{T_I T_A - T_C} \]  

(6.8)

The partial derivatives of \( \eta^* \) with respect to each of the three temperatures are written next. Note that the derivatives are taken with all other temperatures held constant in each case.

\[ \frac{\partial \eta^*}{\partial T_A} = \frac{-T_C(T_I - T_C)}{T_I(T_A - T_C)^2} \]  

(D.1)

\[ \frac{\partial \eta^*}{\partial T_I} = \frac{T_A}{T_I(T_A - T_C)} \]  

(D.2)

\[ \frac{\partial \eta^*}{\partial T_C} = \frac{-T_A(T_A - T_I)}{T_I(T_A - T_C)^2} \]  

(D.3)

Equations D.1 to D.3 were evaluated, as discussed in Section 6.3.4, to obtain the values in Table 16.

For an operating temperature booster, the product temperature is greater than the heat input temperature. Furthermore, the heat input temperature is greater than the heat rejection temperature. For the ideal model these relationships are written as

\[ T_A > T_I > T_C \]  

(D.4)

By examination, the derivatives in Eqs. D.1 to D.3 have
the following characteristics when the relationships in Eq. D.4 are imposed.

\[ \frac{\partial \eta^*}{\partial T_A} < 0 \]  
(D.5)

\[ \frac{\partial \eta^*}{\partial T_I} > 0 \]  
(D.6)

\[ \frac{\partial \eta^*}{\partial T_C} < 0 \]  
(D.7)

Therefore, the conclusions of the discussion in Section 6.3.4 of the effects of temperature on performance are independent of the particular operating point used in the evaluation of the derivatives. The numerical results of Section 6.3.4 are thus shown to be representative of the temperature booster at any operating point which satisfies Eq. 6.4. A similar result is obtained next for the second law performance measure.

D.2 Second Law Performance Measure

The second law performance measure for the ideal cycle is given in Eq. 6.11 which is rewritten here for convenience.
The partial derivatives of $\varepsilon^*$ with respect to the temperatures are written next.

$$
\frac{\partial \varepsilon^*}{\partial T_A} = \frac{T_I - T_C}{T_I - T_0} \frac{(T_C - T_0)}{(T_A - T_C)^2}
$$

$$
\frac{\partial \varepsilon^*}{\partial T_I} = \frac{T_A - T_0}{T_A - T_C} \frac{(T_C - T_0)}{(T_I - T_0)^2}
$$

$$
\frac{\partial \varepsilon^*}{\partial T_T} = \frac{T_T - T_0}{T_T - T_C} \frac{(T_C - T_0)}{(T_I - T_0)^2}
$$

An operating temperature booster must satisfy the relationships in Eq. D.4. When these requirements are imposed on Eqs. D.8 to D.10 the following characteristics are evident by examination.

$$
\frac{\partial \varepsilon^*}{\partial T_A} < 0 \quad \text{(D.12)}
$$

$$
\frac{\partial \varepsilon^*}{\partial T_I} > 0 \quad \text{(D.13)}
$$
The interpretation of these derivatives is discussed in Section 6.3.4 with reference to a particular set of temperatures. Equations D.12 to D.14 indicate that the conclusions based on the particular operating point are general conclusions which are independent of the operating point.

The derivative of $\varepsilon^*$ with respect to the availability reference environment temperature, $T_g$, in Eq. D.11 is included for completeness. For the temperature booster with the relationships in Eq. D.4, Eq. D.11 gives

\[
\frac{\partial \varepsilon^*}{\partial T_g} < 0 \quad (D.14)
\]

for any $T_g$. Since the choice of $T_0$ is arbitrary in the present study, the influence of $T_0$ represented by the derivative in Eq. D.15 is not particularly relevant to the current discussion.
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