

# Improved Property Data Correlations of Absorption Fluids for Computer Simulation of Heat Pump Cycles

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## ABSTRACT

*Substantial amounts of data have been generated over the years on the thermodynamic and transport properties of absorption fluids, based on measurements conducted both in laboratory equipment and in working heat pump systems. In recent years, efforts have been under way to extend the range of available data to higher temperatures and pressures to facilitate implementation of advanced, multistage cycles. The data have been presented in the literature in various forms, including tables, equations of state based on thermodynamic models, and empirical equations, for different ranges.*

*The growing need for computer simulations of absorption systems has prompted the correlation of property data. The objective of the present study has been to compile the most recent available information on common absorption fluids and present it in a form suitable for computer calculations. Considering the fact that modeling a complex cycle may involve a large number of iterations by the simulation program, easy evaluation of the required properties is of utmost importance. In correlating the data, an effort has been made to reduce to a minimum any iterative calculations. Property data correlations have been developed for the fluids most commonly used in absorption systems: water, lithium bromide (LiBr)-water, and water-ammonia. The correlations are based on physical equations of state, relying on thermodynamic models. Correlations are given for vapor-liquid equilibrium (PTX), liquid and vapor enthalpy, liquid density, and vapor entropy. The correlations have been implemented in a computer code for simulation of absorption systems and were found to be both accurate and convenient for calculations.*

## INTRODUCTION

The accelerated development of advanced absorption systems in the last two decades has created a need for reliable and effective computer simulations to predict performance, analyze behavior, and perform parametric studies and various optimiza-

tions. Several system-specific computer models have been developed in recent years that have proven to be valuable tools for research and development and for design optimization. Some of them were validated against experimental data with good agreement. Along with the development of simulation models came the need for property data. Efforts have been under way to correlate existing data on the thermodynamic and transport properties of absorption fluids and extend their range to higher temperatures and pressures to facilitate implementation of advanced, multistage cycles.

System-specific models are restricted in their simulation capability and limited to the particular system for which they were created. Their structure usually does not allow easy modification to model other systems and they generally fit on specific working fluid pair. A computer code has been developed for simulation of absorption systems in a flexible and modular form, making it possible to investigate various cycle configurations with different working fluids (Grossman et al. 1987; Grossman and Wilk 1994). The structure of the code is based on the fact that each absorption system consists of standard components (e.g., absorber, evaporator, generator, condenser, etc.). Each basic component is simulated in the code by a unit subroutine providing a mathematical description of the physics of that component. The unit subroutine contains all the physical equations required to fully simulate its behavior, such as energy balance, conservation of mass for each material species, heat and mass transfer, and thermodynamic equilibrium. The main program calls the unit subroutines and links them together in a form corresponding to the user's specification to form the complete cycle. Each call to a unit subroutine is equivalent to collecting all the equations associated with it, without attempting to solve them as yet. When the calls to all the unit subroutines have been completed, a mathematical solver routine is employed to solve the set of nonlinear equations simultaneously, using an iterative procedure. The output contains the temperature, enthalpy, flow rate, concentration, pressure, and vapor fraction

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at each of the cycle's state points as well as the heat load and transfer characteristics of each unit.

An important part of each simulation code is the thermodynamic properties of working fluids. In the code, where the user can select from a variety of fluids, the properties have been incorporated in the form of a property database external to the unit subroutines. Each unit subroutine, when invoked, calls the database several times and retrieves from it the properties required by its various equations. The separation between the unit subroutines and the property subroutines provides the flexibility for each unit to operate with different working fluids, as specified by the user. In addition, it allows for extending and improving the database without affecting the rest of the program. The structure of the database has been described in detail by Grossman et al. (1987). It presently contains the materials LiBr-H<sub>2</sub>O solution, H<sub>2</sub>O-NH<sub>3</sub> solution and vapor, H<sub>2</sub>O liquid and vapor, LiBr-H<sub>2</sub>O-NH<sub>3</sub> solution, LiBr/ZnBr<sub>2</sub>-CH<sub>3</sub>OH solution, CH<sub>3</sub>OH liquid and vapor, LiNO<sub>3</sub>/KNO<sub>3</sub>/NaNO<sub>3</sub>-H<sub>2</sub>O solution, NaOH-H<sub>2</sub>O solution, and LiCl-H<sub>2</sub>O solution.

The objective of this work has been to update the existing property subroutines for the most common and important absorption fluids—water, LiBr-water, and water-ammonia, according to the latest information available in the literature. In particular, the present data of aqueous lithium bromide solution taken from the *ASHRAE Handbook* (ASHRAE 1989) is not satisfactory, as it covers only LiBr concentrations above 45 wt% and is limited to solution temperatures below 177°C (350°F); with the current interest in double- and triple-effect chillers, higher temperatures are desired. The water-ammonia data taken from Jennings (1981) cover only the saturation range and do not include the superheated range; they also are limited to temperatures below 230°C (446°F). Thus, an important objective is to extend the applicable range of the data in temperature, pressure, and concentration for all the fluids. It is believed that the updated property data will be useful not only in the present database, but also for others interested in extended properties for computer simulations.

Three major features are required from property equations to be suitable for incorporation into the computer simulation code:

1. One particular fluid property should be described by a single equation within the whole desired parameter range. Using different equations for different segments of the parameter range would most likely entail convergence problems in cases where the solution lies close to the border between two subparameter ranges; the solver would then be compelled to switch between different equations during the iteration process.
2. The transition from one property equation to another should be smooth, e.g., a property equation for a superheated or subcooled fluid should convert to the respective property equation for the saturated fluid when temperature and pressure approach saturation values; a property equation of a mixture should reduce to the respective property

equation of its component when the component's concentration approaches 100%. The reason for this requirement is again expected convergence problems in cases where the solution of the simulation lies close to a concentration value of zero, forcing the solver to switch between different equations during the iteration process.

3. All equations should be explicit in the property in question to avoid additional iterations during calls to the property database.

Equations that meet the above requirements will be selected and analyzed with respect to their accuracy and applicability to the broadest possible parameter ranges. The selected equations will be implemented in the existing property database of the computer simulation code.

## PROPERTIES OF PURE WATER

Various correlations for the properties of saturated liquid water and saturated water vapor can be found in the literature (Irvine and Liley 1984; Saul and Wagner 1987). However, the correlations of Irvine and Liley (1984) cannot be applied for the present purpose for two reasons: (1) Most saturation properties are covered by two or more separate equations, each valid only in a limited parameter range. Using these equations in a simulation program package that conducts iterations of any kind will most likely entail convergence problems in cases where the solution of the simulation lies close to the border of a parameter range and will compel the solver to switch between these different equations during the iteration process. (2) Different equations are proposed for the saturation pressure as a function of the temperature  $p_s = f(t)$  and its inverse, the saturation temperature as a function of the pressure,  $t_s = f(p)$ , a fact that may well cause similar convergence problems during iteration as described above. Hence, the correlations from Saul and Wagner (1987) are used for calculating all saturation properties. Equations for the properties of superheated water vapor had to be developed based on the correlations from Irvine and Liley (1984) to obtain consistency with the saturation properties of Saul and Wagner (1987).

## Properties of Saturated Water

The equations for vapor pressure, enthalpies ( $h'$ ,  $h''$ ), entropies ( $s'$ ,  $s''$ ), and densities ( $\rho'$ ,  $\rho''$ ) of saturated liquid water and water vapor (Saul and Wagner 1987) cover the entire range of vapor-liquid equilibrium from the triple point to the critical point. They have been approved by the International Association for the Properties of Steam (IAPS) 1986. As they have been published before in a rather comprehensive form by Saul and Wagner (1987), there is no need to present them here again.

## Properties of Superheated Water Vapor

Properties of superheated water vapor can be found (Irvine and Liley 1984) in the form of tables and correlations. However, the correlations cannot be applied directly for the present purpose as they are based on the respective correlations for saturated vapor, which give results slightly different from those

obtained by Saul and Wagner (1987).<sup>1</sup> Using these equations in the program package will most likely entail convergence problems in cases where the state of the vapor is close to saturation; the solver would then be compelled to switch from the saturated vapor equation to the superheated vapor equation during the iteration process. Hence, there was a need to develop enthalpy and entropy equations for superheated vapor that are consistent with the chosen saturated vapor equations.

Applying Irvine and Liley's (1984) superheated vapor equations for calculating the enthalpies  $h(p, t)$  and  $h(p, t_s(p))$  and the entropies  $s(p, t)$  and  $s(p, t_s(p))$  leads to the expressions:

$$c_{p,v} = \frac{h(p, t) - h(p, t_s)}{t - t_s} = E_1 + E_2(T + T_s) + \frac{F_1}{T - T_s} \left( 1 - \exp\left(\frac{T_s - T}{45}\right) \right) \quad (1)$$

where

$$E_1 = e_0 + e_1 p + e_2 p^2$$

$$E_2 = e_3 + e_4 p + e_5 p^2$$

$$F_1 = f_0 + f_1 T_s + f_2 T_s^2 + f_3 T_s^3 + f_4 T_s^4$$

and

$$s(p, t) - s(p, t_s) = g_1(T - T_s) + g_2(T^2 - T_s^2) + g_3(T^3 - T_s^3) + g_4(T^4 - T_s^4) + (h_0 + h_1 T_s + h_2 T_s^2 + h_3 T_s^3 + h_4 T_s^4) \left( 1 - \exp\left(\frac{T_s - T}{85}\right) \right) \quad (2)$$

The numerical values of the coefficients  $e_i$ ,  $f_i$ ,  $g_i$ , and  $h_i$  are given in Table 1. Note that temperatures,  $T$ , have to be pro-

vided in K and pressures,  $p$ , in MPa, leading to  $c_{p,v}$  and  $s$  in kJ/kg·K.

Using Equations 1 and 2 allows the calculation of  $h(t, p)$  from

$$h(p, t) = h''(p) + c_{p,v}(t - t_s(p)) \quad (3)$$

and of  $s(t, p)$  from

$$s(p, t) = s''(p) + (s(p, t) - s(p, t_s(p))), \quad (4)$$

which are consistent with the respective saturation properties in cases when  $t_s(p)$ ,  $h''(p)$ , and  $s''(p)$  are taken from Saul and Wagner (1987). It is evident that the accuracy of the numerical enthalpy and entropy values obtained with the described approach strongly depends on the accuracy of the saturation properties from Irvine and Liley with respect to those from Saul and Wagner. The correlations of both authors agree well, with a maximum deviation in the enthalpy of less than 1 kJ/kg. This proves that the proposed approach gives results that can be regarded as sufficiently accurate for the present purpose.

## PROPERTIES OF AQUEOUS LITHIUM BROMIDE SOLUTION

Various correlations for the properties of saturated aqueous lithium bromide solution can be found in the literature (McNeely 1979; Brunk 1982; Patterson and Perez-Blanco 1988; Lénard et al. 1992; Feurecker et al. 1993; Peters and Keller 1994). McNeely (1979) compiled vapor pressure and enthalpy data from Pennington (1955) and Löwer (1960) and additional data were provided by various industrial companies in the range  $0 \leq t \leq 180^\circ\text{C}$ ,  $0 \leq \xi_{\text{LiBr}} \leq 70\%$  in the form of tables. He developed correlations for the boiling point temperature  $t = f(p, \xi_{\text{LiBr}})$ , valid within the range  $5 \leq t \leq 175^\circ\text{C}$ ,  $45 \leq \xi_{\text{LiBr}} \leq 70\%$ , and for the enthalpy  $h = f(t, \xi_{\text{LiBr}})$ , valid within the range  $15 \leq t \leq 165^\circ\text{C}$ ,  $40 \leq \xi_{\text{LiBr}} \leq 70\%$ , based on these data. These equations are recom-

1. Irvine and Liley base their equations on the critical temperature  $T_c = 647.3$  K as opposed to the more recent value  $T_c = 647.14$  K by Saul and Wagner.

TABLE 1 Numerical Values of the Coefficients  $e$ ,  $f$ ,  $g$ , and  $h$  in Equations 1 and 2

	e	f	g	h
0	+ 1.610693	+ 1.707820 $10^3$		+ 1.777804
1	+ 5.472051 $10^{-2}$	- 1.699419 $10^1$	+ 1.039008 $10^{-2}$	- 1.802468 $10^{-2}$
2	+ 7.517537 $10^{-4}$	+ 6.2746295 $10^{-2}$	- 9.873085 $10^{-6}$	+ 6.854459 $10^{-5}$
3	+ 3.383117 $10^{-4}$	- 1.0284259 $10^{-4}$	+ 5.434110 $10^{-9}$	- 1.184424 $10^{-7}$
4	- 1.975736 $10^{-5}$	+ 6.4561298 $10^{-8}$	- 1.170465 $10^{-12}$	+ 8.142201 $10^{-11}$
5	- 2.874090 $10^{-7}$			

mended in the *ASHRAE Handbook* (ASHRAE 1989)<sup>2</sup> to be used in the design of absorption heat pump equipment.

Brunk (1982) published an improved boiling point temperature correlation for a broader parameter range  $5 \leq t \leq 180^\circ\text{C}$ ,  $0 \leq \xi_{\text{LiBr}} \leq 70\%$  based on McNeely's tables. In addition, he developed an enthalpy correlation by fitting the data of Löwer (1960) for the parameter range  $15 \leq t \leq 165^\circ\text{C}$ ,  $0 \leq \xi_{\text{LiBr}} < 40\%$  that is not covered by McNeely's enthalpy equation. Brunk also gives an equation for the density of saturated solution in the range  $0 \leq t \leq 100^\circ\text{C}$ ,  $0 \leq \xi_{\text{LiBr}} \leq 70\%$  (excluding concentrations below 15% at temperatures above  $70^\circ\text{C}$ ) based on the data of Löwer, and an equation for the crystallization temperature in the concentration range  $47.9 \leq \xi_{\text{LiBr}} \leq 75\%$ . Patterson and Perez-Blanco (1988) derived equations for the boiling point temperature in the range  $0 \leq t \leq 180^\circ\text{C}$ ,  $0 \leq \xi_{\text{LiBr}} \leq 70\%$ , for the enthalpy in the range  $0 \leq t \leq 180^\circ\text{C}$ ,  $0 \leq \xi_{\text{LiBr}} \leq 70\%$ , both based on the database of McNeely (1979), and for the density in the range  $0 \leq t \leq 100^\circ\text{C}$ ,  $10 \leq \xi_{\text{LiBr}} \leq 60\%$ , based on the data of Uemura (1975).

Lee et al. (1990) measured densities of saturated aqueous lithium bromide solution in the range  $25 \leq t \leq 200^\circ\text{C}$ ,  $45 \leq \xi_{\text{LiBr}} \leq 60\%$  and developed a correlation by fitting these data. In addition, they included data available in the literature to develop a second correlation that covers a wider parameter range, i.e.,  $120 \leq t \leq 210^\circ\text{C}$ ,  $44 \leq \xi_{\text{LiBr}} \leq 65\%$ . Lénard et al. (1992) measured vapor pressures at high temperatures and high concentrations. They fitted their experimental results in the range  $120 \leq t \leq 210^\circ\text{C}$ ,  $44 \leq \xi_{\text{LiBr}} \leq 65\%$ .

Feuerecker et al. (1993) measured boiling point data and fitted their experimental results in the range  $45 \leq t \leq 190^\circ\text{C}$ ,  $40 \leq \xi_{\text{LiBr}} \leq 76\%$ . In addition, they measured the specific heat of saturated solution, which allowed them to calculate a set of enthalpy values that they fitted in the range  $10 \leq t \leq 190^\circ\text{C}$ ,  $40 \leq \xi_{\text{LiBr}} \leq 75\%$  at vapor pressures of less than 200 kPa. They employed for this purpose a density correlation that is valid for  $10 \leq \xi_{\text{LiBr}} \leq 80\%$ . Peters and Keller (1994) developed a semi-empirical thermodynamic model to fit the VLE data published by Pennington (1955), Löwer (1960), Renz (1980), Zimmermann (1991), and Feuerecker et al. (1993) in the range  $0 \leq t \leq 190^\circ\text{C}$ ,  $5 \leq \xi_{\text{LiBr}} \leq 76\%$ . The claimed advantage of this model is that it allows one to extrapolate measured VLE data, at least to a certain extent.

### Boiling Point Temperature and Vapor Pressure of Aqueous Lithium Bromide Solution

The empirical equations of McNeely (1979), Brunk (1982), and Feuerecker et al. (1993) for the boiling temperature of saturated aqueous lithium bromide solution as a function of the pressure and the concentration are fits in the form of Dühring lines:

$$t(p, \xi_{\text{LiBr}}) = A(\xi_{\text{LiBr}}) + B(\xi_{\text{LiBr}}) \cdot t_s(p) \quad (5)$$

where  $t_s$  is the saturation temperature of pure water at the pressure  $p$ . McNeely and Brunk give  $A$  and  $B$  as cubic polynomials in  $\xi_{\text{LiBr}}$  with four fitted coefficients each, whereas Feuerecker et al. give expressions for  $A$  and  $B$  that contain the LiBr/H<sub>2</sub>O mole ratio with fractional exponents from 1/2 to 4/2, arranged in sums with five fitted coefficients each. Patterson and Perez-Blanco (1988) fitted their data with the equation

$$t_s(p) = A(t) + B(t) \cdot \xi_{\text{LiBr}} + C(t) \cdot \xi_{\text{LiBr}}^2 \quad (6)$$

where  $t_s$  is the saturation temperature of pure water at the pressure  $p$ , and  $A$ ,  $B$ , and  $C$  are quadratic polynomials in  $t$  with three fitted coefficients each. Lénard et al. (1992) chose the semi-empirical equation

$$p(t, \xi_{\text{LiBr}}) = (\Psi_H + \Psi_H(1 - \Psi_H) \cdot A(t, \Psi_H)) \cdot p_s(t), \quad (7)$$

which is suitable for correlating vapor pressures of aqueous electrolyte solutions to fit their data. The saturation pressure of pure water,  $p_s$ , is taken at the temperature  $t$ ,  $\Psi_H$  is the mole concentration of water in the solution with respect to the total number of particles when assuming complete dissociation of all LiBr molecules, and  $A$  stands for an algebraic function in  $t$  and  $\Psi_H$ .

Peters and Keller (1994) correlated their data by means of a semi-empirical thermodynamic model as opposed to the purely empirical models leading to Equations 5 and 6. They obtain the equation

$$p(t, \xi_{\text{LiBr}}) = \gamma_H \cdot \Psi_H \cdot p_s(t) \quad (8)$$

from the theory of thermodynamics of mixtures. In addition, they introduce a so-called "solvation model" that assumes that LiBr, after being dissolved in water, partially dissociates. The Li<sup>+</sup> and Br<sup>-</sup> ions generated in this way are immediately coated with water molecules, forming ionic clusters that are considered new components in the thermodynamic sense. Hence, the mole concentration,  $\Psi_H$ , and the activity coefficient of water,  $\gamma_H$ , in Equation 8 refer to the number of remaining free water molecules in the solution after formation of the clusters. Both quantities follow from a system of four highly nonlinear coupled equations that has to be solved iteratively. A further detailed description of this model is beyond the scope of this work and the interested reader is referred to Peters and Keller (1994).

The advantage Equations 5 and 6 have in common is that they allow for explicit calculation of both the boiling temperature as a function of pressure and concentration, and the vapor pressure as a function of temperature and concentration without any iterative procedure. Being explicit is regarded as a major requirement for using working-fluid property equations in the existing computer code that already includes a heavily iterative solver. However, Equations 5 and 6 cannot be recommended for use in the code for various reasons. The models of McNeely (1979) and Feuerecker et al. (1993) cover only concentrations above 45% and 40%, respectively. Brunk proposes three different equations

2. Note that the coefficient  $D$  on page 17.70 of the 1989 *ASHRAE Handbook—Fundamentals*, SI Edition, should read correctly  $D = -1603.54$  (as opposed to the given value  $D = -1596.49$ ) to be consistent with the I-P Edition.

to cover the whole desired concentration range, a fact that may well entail similar convergence problems during iteration, as described in the previous section. The equation of Patterson and Perez-Blanco is valid for the whole concentration range, but it was developed by utilizing a limited experimental data set, i.e., only the data published by McNeely.

Equation 7 cannot be recommended as it is valid only at temperatures above 120°C and at concentrations above 44%. Additionally, it is explicit only in the vapor pressure in  $p = f(t, \xi_{\text{LiBr}})$  but not in the boiling temperature  $t = f(p, \xi_{\text{LiBr}})$ . The model of Peters and Keller (Equation 8) cannot be recommended from the standpoint of "computer friendliness" as it includes a system of nonlinear equations that requires iterative solution. Yet, it was developed with the broadest and most up-to-date set of experimental data and the correlation is based on a thermodynamic model rather than a mere mathematical formula with no physical basis. Therefore, the model of Peters and Keller has been selected in this work as the basis for developing a novel, improved explicit equation.

The foregoing discussion has explained why none of the existing equations for the boiling point temperature and the vapor pressure of saturated aqueous lithium bromide solution should be incorporated into the existing computer code. The objective of this work is to develop a new correlation that covers the whole desired concentration and temperature range, and is explicit in both temperature as a function of pressure and concentration, and pressure as a function of temperature and concentration. To accomplish this, a database of 1,320 points was generated by calculating the vapor pressure of saturated aqueous lithium bromide solution at concentrations between 5% and 76% and at temperatures between 0°C and 190°C by means of the model of Peters and Keller (Equation 8). This database represents 388 measured VLE data points by Pennington (1955), Löwer (1960), Renz (1980), Zimmermann (1991), and Feuerecker et al. (1993) with a mean deviation in the vapor pressure of 1.6%, as does the model of Peters and Keller itself. The numerically generated data were fitted by Dühring lines according to Equation 5 with the polynomials  $A$  and  $B$  following from

$$\begin{aligned} A &= \sum_{i=0}^{10} a_i \cdot \xi_{\text{LiBr}}^i \\ B &= \sum_{i=0}^{10} b_i \cdot \xi_{\text{LiBr}}^i \end{aligned} \quad (9)$$

The coefficients  $a_i$  and  $b_i$  are listed in Table 2. They were calculated by minimizing the maximum absolute deviation between the temperatures that follow from the correlation and the temperatures of the database at all 1,320 considered data points, as dependent upon  $(p, \xi_{\text{LiBr}})$

$$\left| t_j^{\text{data}}(p, \xi_{\text{LiBr}}) - t_j^{\text{corr}}(p, \xi_{\text{LiBr}}) \right|_{\text{max}} = \min \quad (10)$$

It is evident that the polynomials  $A(\xi_{\text{LiBr}} = 0)$  and  $B(\xi_{\text{LiBr}} = 0)$  have to attain the values 0.0 and 1.0, respectively, to accomplish a smooth transition from the property equation of lithium

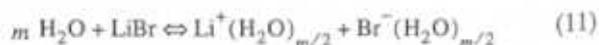
bromide/water solution to the property equation of pure water. Hence, the coefficients  $a_0$  and  $b_0$  were set to 0.0 and 1.0, respectively, and were not fitted as done by Brunk (1982) and Patterson and Perez-Blanco (1988). The largest temperature deviation between the correlation and the database at the 1,320 data points is no more than 0.6 K.

Figure 1 shows the boiling point temperatures of aqueous lithium bromide solution at different concentrations according to the various proposed correlations in comparison with the values given by the model of Peters and Keller (1994). At low concentrations (10% and 25%), the correlations of Brunk (1982), Patterson and Perez-Blanco (1988) (at 25% only below 150°C), and the one developed in this work are sufficiently accurate, while the remaining correlations cannot be recommended. At a concentration of 40% all equations give good results, except that of McNeely (1979) and that of Lénard et al. (1992) above 150°C. At a concentration of 55% all correlations give accurate results, except for the equation of Lénard et al., which is valid only at temperatures above 120°C. At a concentration of 70% none of the published correlations approach the correct boiling temperature closer than some 3 K, except for the equation of Lénard et al. and the one developed in this work. These five examples illustrate that only the new equation developed in this work gives satisfactory results within the whole desired parameter range, that is,  $0 \leq t \leq 190^\circ\text{C}$ ,  $0 \leq \xi_{\text{LiBr}} \leq 76\%$ .

## Enthalpy of Saturated Aqueous Lithium Bromide Solution

**Enthalpy from Activity Coefficients** Peters and Keller (1994) developed a semi-empirical thermodynamic model of aqueous lithium bromide solution to correlate their experimental VLE data. This model was applied successfully to the prediction of the solution vapor pressure as a function of concentration and temperature, as shown in the previous section. The fact that their data correlating procedure includes the fitting of activity coefficients gives reason to believe that the model also may be employed for calculating caloric solution properties. The objective of this section is to examine their model with respect to the possibility of calculating the solution enthalpy.

According to the model, the solution consists of three components in the thermodynamic sense: water molecules, lithium bromide molecules, and clusters of  $\text{Li}^+$  and  $\text{Br}^-$  ions, each coated by a variable number of water molecules. The dissociation process generating the ionic clusters is described by the chemical reaction equation



with the so-called solvation number of the reaction

$$m = 4 - 5 \cdot \psi_{\text{LiBr}} \quad (12)$$

where  $\psi_{\text{LiBr}}$  denotes the molar lithium bromide concentration before the dissociation. Considering the above three components, the molar Gibbs free energy of the solution is given by

TABLE 2 Numerical Values of Coefficients *a* and *b* in Equation 9

i	a	b
0	0.0	1.0
1	+ 1.6634856 10 <sup>+1</sup>	- 6.8242821 10 <sup>-2</sup>
2	- 5.5338169 10 <sup>+2</sup>	+ 5.8736190 10 <sup>0</sup>
3	+ 1.1228336 10 <sup>+4</sup>	- 1.0278186 10 <sup>+2</sup>
4	- 1.1028390 10 <sup>+5</sup>	+ 9.3032374 10 <sup>+2</sup>
5	+ 6.2109464 10 <sup>+5</sup>	- 4.8223940 10 <sup>+3</sup>
6	- 2.1112567 10 <sup>+6</sup>	+ 1.5189038 10 <sup>+4</sup>
7	+ 4.3851901 10 <sup>+6</sup>	- 2.9412863 10 <sup>+4</sup>
8	- 5.4098115 10 <sup>+6</sup>	+ 3.4100528 10 <sup>+4</sup>
9	+ 3.6266742 10 <sup>+6</sup>	- 2.1671480 10 <sup>+4</sup>
10	- 1.0153059 10 <sup>+6</sup>	+ 5.7995604 10 <sup>+3</sup>

$$g^m = \psi_H g_H^m + \psi_L g_L^m + 2\psi_C g_C^m + \Delta g_{mix}^m + \Delta g^m \quad (13)$$

with the molar excess Gibbs free energy

$$\Delta g^m = RT[\psi_H \ln \gamma_H + \psi_L \ln \gamma_L + 2\psi_C \ln \gamma_C] \quad (14)$$

$\Delta g_{mix}^m$  is the molar Gibbs free energy of mixing;  $g_H^m$ ,  $g_L^m$ , and  $g_C^m$  are reference molar Gibbs free energies of the components (in pure state or at infinite dilution);  $\psi_H$ ,  $\psi_L$ , and  $\psi_C$  are the molar concentrations of the components after dissociation; and  $\gamma_H$ ,  $\gamma_L$ , and  $\gamma_C$  are the activity coefficients of the components in the solution. The molar solution enthalpy follows by dividing Equation 13 by the temperature, forming the derivative with respect to the temperature at constant pressure and concentrations, and substituting

$$h^m = -T^2 \left( \frac{\partial (g^m/T)}{\partial T} \right)_{p, \psi_i} \quad (15)$$

and

$$h_i^m = -T^2 \left( \frac{\partial (g_i^m/T)}{\partial T} \right)_p$$

to be

$$h^m = \psi_H h_H^m + \psi_L h_L^m + 2\psi_C h_C^m + \Delta h^m \quad (16)$$

with the molar excess enthalpy

$$\Delta h^m = -RT^2 \left[ \psi_H \left( \frac{\partial (\ln \gamma_H)}{\partial T} \right)_{p, \psi_i} + \psi_L \left( \frac{\partial (\ln \gamma_L)}{\partial T} \right)_{p, \psi_i} + 2\psi_C \left( \frac{\partial (\ln \gamma_C)}{\partial T} \right)_{p, \psi_i} \right] \quad (17)$$

and the reference enthalpies of the components  $h_H^m$ ,  $h_L^m$ , and  $h_C^m$ .

The first obstacle encountered when employing Equation 16 is to obtain the reference enthalpies of the components. Neither water nor lithium bromide exists in the present temperature and pressure range as a pure fluid, and pure "ionic cluster fluids" do not exist at all. However, the reference enthalpy of the clusters can be eliminated from Equation 16 by making use of the equilibrium condition of the dissociation reaction (Equation 11) in the form

$$2g_C^m = mg_H^m + g_L^m - RT \ln \frac{(\psi_C \gamma_C)^2}{(\psi_H \gamma_H)^m (\psi_L \gamma_L)} \quad (18)$$

Dividing this expression by the temperature, forming the derivative with respect to the temperature at constant pressure and concentrations, and considering Equation 15 yields the molar reference cluster enthalpy,

$$2h_C^m = mh_H^m + h_L^m + \Delta h_{diss}^m \quad (19)$$

as a function of the molar reference enthalpies of water and lithium bromide, and the molar dissociation enthalpy:

$$\Delta h_{diss}^m = -RT^2 \left[ m \left( \frac{\partial (\ln \gamma_H)}{\partial T} \right)_{p, \psi_i} + \left( \frac{\partial (\ln \gamma_L)}{\partial T} \right)_{p, \psi_i} - 2 \left( \frac{\partial (\ln \gamma_C)}{\partial T} \right)_{p, \psi_i} \right] \quad (20)$$

Substituting Equation 19 into Equation 16 leads to

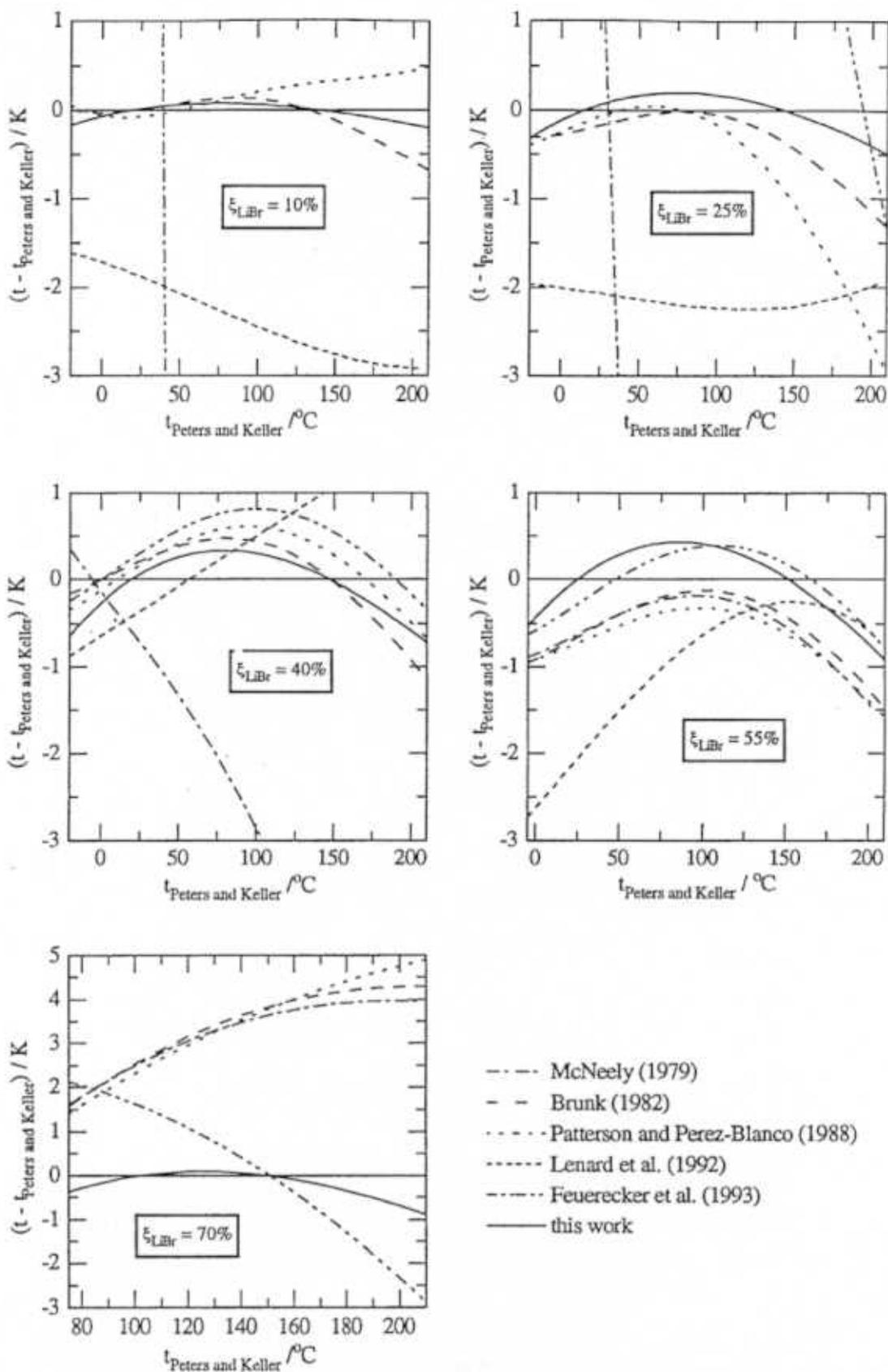


Figure 1 Boiling point temperatures of aqueous lithium bromide solution from different correlations compared to the model of Peters and Keller (1994).

$$h^m = (\psi_H + m\psi_C)h_H^m + (\psi_L + \psi_C)h_L^m + \psi_C\Delta h_{diss}^m + \Delta h^m. \quad (21)$$

This expression allows one to calculate the solution enthalpy from the reference enthalpies of water and lithium bromide, the molar concentrations of the components after the dissociation, and the activity coefficients of the components. The molar reference enthalpy of water can be set equal to the molar enthalpy of pure saturated liquid water at the temperature  $T$ , when neglecting its pressure dependence. The molar reference enthalpy of lithium bromide is not available. However, assuming it to be independent of pressure and concentration, one may obtain it from Equation 21 as a function of the temperature by introducing the solution enthalpy  $h^m$  from reliable measurements at the appropriate temperatures.

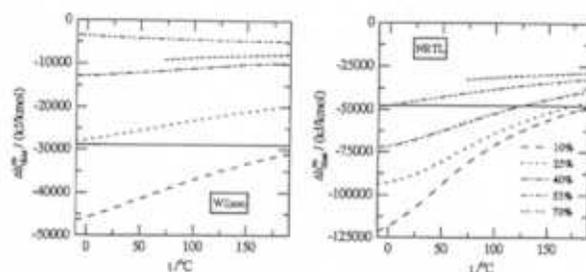
The second difficulty encountered when employing the model for calculating the solution enthalpy is how to obtain the activity coefficient derivatives at constant pressure and concentrations that are required in Equation 17 for the molar excess enthalpy and in Equation 20 for the molar dissociation enthalpy. Peters and Keller (1994) provide activity coefficients only at VLE. Thus, formulation of the derivatives with respect to temperature at constant concentrations implies inevitably varying pressure according to the Dühring lines. However, these derivatives may be used in Equations 17 and 20, assuming pressure-independent activity coefficients in the liquid region.

It was attempted in this work to employ the above set of equations in conjunction with the fitted activity coefficients of Peters and Keller (1994) for calculating the enthalpy of saturated aqueous lithium bromide solution. The lithium bromide reference enthalpy/temperature function was determined from Equation 21 by using solution enthalpies published by Feurecker et al. (1993). The function was expected to be independent of the lithium bromide mass concentration at which the solution enthalpies were taken. However, it was recognized that significantly different reference enthalpy/temperature functions were obtained when using solution enthalpies at identical temperatures but at different lithium bromide mass concentrations in the range  $40 \leq \xi_{LiBr} \leq 75\%$ . Further detailed examinations of the thermodynamic model were required, namely with respect to the consistency of the fitted activity coefficients, to illuminate this phenomenon.

During development of their model, Peters and Keller (1994) made use of the equilibrium condition of the dissociation reaction in form of the van't Hoff relation:

$$K_C = K_C^o \exp\left[-\frac{\Delta h_{diss}^m}{RT}\right] = \frac{(\psi_C \gamma_C)^2}{(\psi_H \gamma_H)^m (\psi_L \gamma_L)}, \quad (22)$$

where  $K_C$  is the equilibrium constant, and  $K_C^o = 0.022$  and  $\Delta h_{diss}^m = -28936.3818$  kJ/kmol are fitted constants. Forming the derivative with respect to the temperature of this relation for constant pressure and concentrations again yields Equation 20. Hence, the right-hand side of Equation 20 must equal the fitted constant value of the molar dissociation enthalpy for all temperatures and concentrations.



**Figure 2** Molar dissociation enthalpy at different lithium bromide mass concentrations and temperatures as obtained from the thermodynamic model when employing the Wilson equations and the NRTL approach, respectively.

This can be verified easily. The temperature deviations of the activity coefficients required in Equation 20 follow from the Wilson equations (which Peters and Keller [1994] employed for correlating their VLE data) in a straightforward, analytical manner. The left-hand side of Figure 2 illustrates the deviation between the molar dissociation enthalpy (as calculated from the activity coefficient derivatives at different lithium bromide mass concentrations and temperatures) and the fitted constant value. The observed large deviations of up to 25,000 kJ/kmol give reason to assume that Peters and Keller's data fit produced thermodynamically inconsistent results. This may be attributed to the fact that the measured VLE data of the three-component system (water molecules, lithium bromide molecules, and clusters) were fitted by means of a model consisting of a single VLE condition, namely, water vapor being in equilibrium with the liquid water in the solution. Thus, the constants in the Wilson equations and in the van't Hoff relation were fitted merely with respect to the water activity ( $\psi_H \cdot \gamma_H$ , see Equation 8). The molar concentrations after dissociation— $\psi_H$ ,  $\psi_L$ , and  $\psi_C$ —and the activity coefficients  $\gamma_H$ ,  $\gamma_L$ , and  $\gamma_C$ , which are additional results of the data-fitting procedure, apparently do not represent valid physical information of the system.

This conclusion is supported by the results of a comparison between the data fit employing the thermodynamic model in conjunction with the Wilson equations (Peters and Keller 1994) and the data fit employing the same model, but in conjunction with the NRTL approach (Peters 1994). The right-hand side of Figure 2 illustrates that the molar dissociation enthalpies, as calculated from the activity coefficient derivatives according to the NRTL approach, differ considerably from the fitted constant value  $\Delta h_{diss}^m = -47696.05$  kJ/kmol, which itself is significantly different from the value obtained when using the Wilson equations.

The molar concentrations, after dissociation yielded by the two, show mostly moderate deviations of less than 0.1 kmol/kmol. As opposed to that, the lithium bromide activity coefficients and the cluster activity coefficients that follow from the

two different approaches differ considerably, with maximum deviations on the order of up to 0.6. They evidently do not contain any valid physical information about the contribution of each component to the caloric properties of the solution. Hence, calculation of the molar solution enthalpy after Equation 21 in conjunction with Equation 17 for the molar excess enthalpy and Equation 20 for the molar dissociation enthalpy must be regarded as impossible. However, both approaches yield almost identical water activities  $\psi_H \cdot \gamma_H$  and solution saturation pressures. This verifies the virtue of both approaches to predict the solution saturation pressure as a function of temperature and concentrations, as was the objective of the development of the model.

**Enthalpy from Specific Heat Measurements** The empirical equations of McNeely (1979), Brunk (1982), and Patterson and Perez-Blanco (1988) for the enthalpy of saturated aqueous lithium bromide solution are all based on the data tables published by McNeely (1979) and Löwer (1960). Their form is given by the formula

$$h(t, \xi_{\text{LiBr}}) = \sum_{i=0}^m \sum_{j=0}^n a_{ij} \xi_{\text{LiBr}}^i t^j \quad (23)$$

where the values of the upper limits  $m$  and  $n$  vary from author to author. Kuck (1994) fitted the enthalpy data of McNeely (1979) in the entire parameter range  $0 \leq t \leq 180^\circ\text{C}$ ,  $0 \leq \xi_{\text{LiBr}} \leq 70\%$  with an approach similar to that in Equation 21:

$$h(t, \xi_{\text{LiBr}}) = \xi_{\text{LiBr}} \cdot h_{\text{LiBr}}(t) + (1 - \xi_{\text{LiBr}}) \cdot h'(t) + \Delta h(t, \xi_{\text{LiBr}}) \quad (24)$$

with

$$\frac{h_{\text{LiBr}}}{\text{kJ/kg}} = \sum_{i=0}^4 a_i \left(\frac{t}{^\circ\text{C}}\right)^i$$

$$\frac{\Delta h}{\text{kJ/kg}} = \xi_{\text{LiBr}}(1 - \xi_{\text{LiBr}}) \sum_{i=0}^4 \sum_{j=0}^3 b_{ij} (2\xi_{\text{LiBr}} - 1)^j \left(\frac{t}{^\circ\text{C}}\right)^i$$

The structure of this equation, where the first term on the right represents the contribution of the enthalpy of the salt, the second term represents the contribution of the enthalpy of the water, and the third term represents the excess enthalpy, guarantees a smooth transition to the values of the pure water enthalpy  $h'(t)$  after Equation 9 for lithium bromide concentrations approaching zero. The numerical values of the coefficients  $a_i$  and  $b_{ij}$  are given in Table 3.

Feuerecker et al. (1993) developed a correlation similar to Equation 23 for lithium bromide mass concentrations above 40% by fitting enthalpy data that were numerically generated based on their specific heat measurements. Figure 3 illustrates that McNeely's data (1979) agree well with Feuerecker's recent measurements. Most of McNeely's enthalpy values lie in the accuracy range that Feuerecker states for his correlation, with some minor exceptions at low temperatures. Hence, McNeely's data table can be regarded as a basis for enthalpy correlations, of the kind developed by the mentioned references, that is sufficiently accurate for the present purpose.

Only two out of the five enthalpy correlations presented here are suitable for implementation into the computer code. The equations of McNeely (1979) and Feuerecker et al. (1993) are valid only at lithium bromide concentrations above 45% and 40%, respectively. Brunk (1982) developed his correlation based on the data of Löwer (1960) for concentrations below 40% and recommends using McNeely's equation for higher concentrations. As already pointed out, the use of a fluid property basis that requires switching between different equations should be strictly avoided to prevent convergence problems in the solver of the code. The equation of Patterson and Perez-Blanco (1988) and the correlation of Kuck (1994) remain the only ones that are considered for use in the code. Figure 4 shows a comparison of their correlations with the data of McNeely (1979) for four lithium bromide concentrations. It is evident that the equation of Kuck gives slightly better results than the equation of Patterson and Perez-Blanco for all concentrations. As Kuck's equation has the additional advantage of allowing for a smooth transition to the enthalpy equation of pure water for  $\xi_{\text{LiBr}} \rightarrow 0$ , it was selected to be incorporated into the computer simulation code.

TABLE 3 Numerical Values of the Coefficients  $a$  and  $b$  in Equation 24

$i$	$a_i$	$b_{i0}$	$b_{i1}$	$b_{i2}$	$b_{i3}$
0	+5.08668 $10^{+2}$	-1.02161 $10^{+3}$	+3.68773 $10^{+1}$	-1.86051 $10^{-1}$	-7.51277 $10^{-6}$
1	-1.86241 $10^{+1}$	-5.33308 $10^{+2}$	+4.02847 $10^{+1}$	-1.91198 $10^{-1}$	0.0
2	+9.85946 $10^{-2}$	+4.83628 $10^{+2}$	+3.99142 $10^{+1}$	-1.99213 $10^{-1}$	0.0
3	-2.50979 $10^{-5}$	+1.15513 $10^{+3}$	+3.33572 $10^{+1}$	-1.78258 $10^{-1}$	0.0
4	+4.15801 $10^{-8}$	+6.40622 $10^{+2}$	+1.31032 $10^{+1}$	-7.75101 $10^{-2}$	0.0

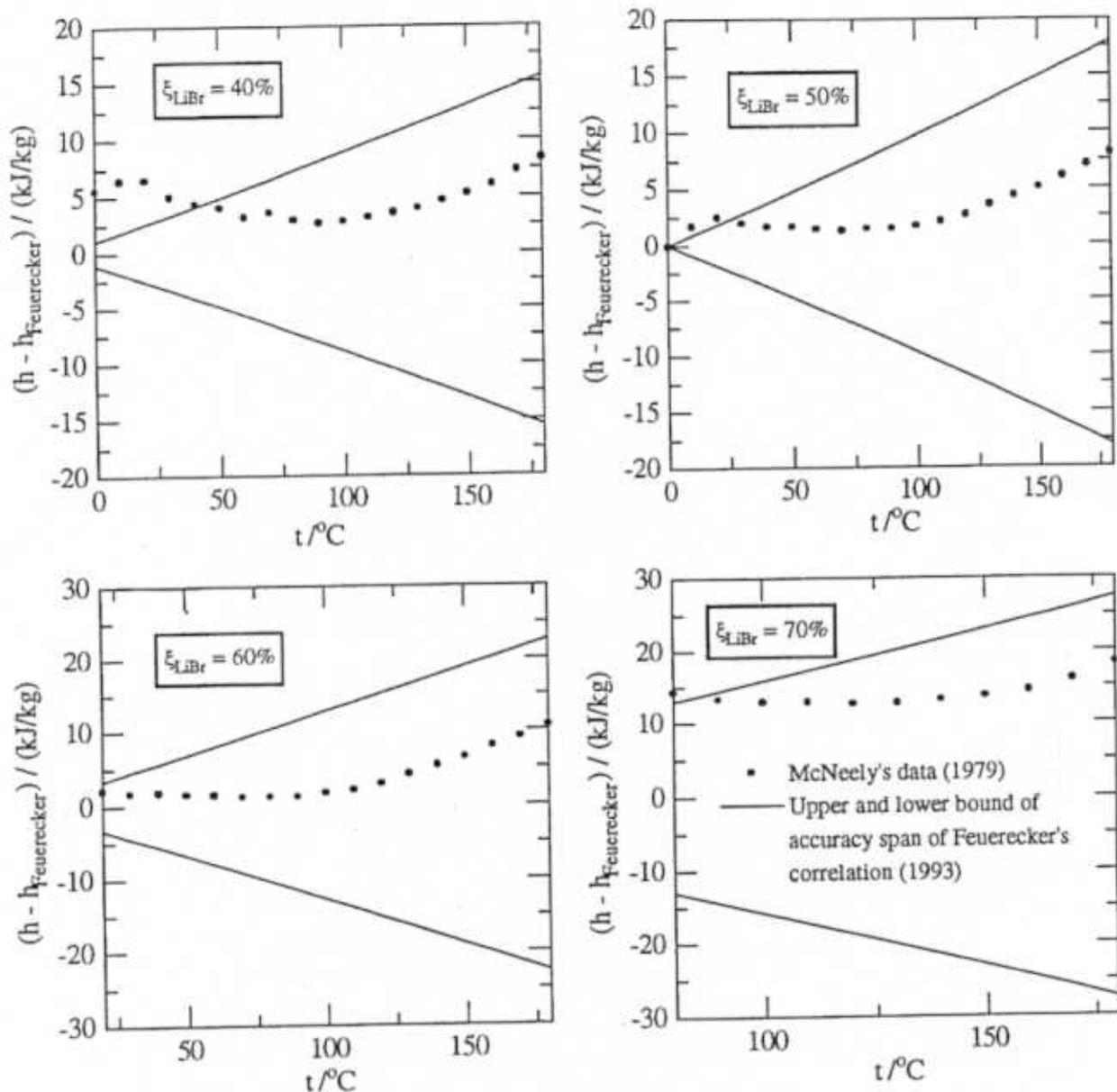


Figure 3 Enthalpy data of saturated aqueous lithium bromide solution after McNeely (1979) compared to the correlation of Feuerecker (1993).

### Density of Saturated Aqueous Lithium Bromide Solution

The correlations of Brunk (1982) and Patterson and Perez-Blanco (1988) for the density of saturated aqueous lithium bromide solution are valid only at temperatures below 100°C. Lee et al. (1990) developed the correlation

$$\frac{\rho}{\text{kg/m}^3} = 1145.36 + 470.84 \cdot \xi_{\text{LiBr}} + 1374.79 \cdot \xi_{\text{LiBr}}^2 - (0.333393 + 0.571749 \cdot \xi_{\text{LiBr}}) \frac{T}{K} \quad (25)$$

based on their own experiments and additional data taken from the literature. This equation is valid in the parameter range  $0 \leq t \leq 200^\circ\text{C}$ ,  $20 \leq \xi_{\text{LiBr}} \leq 65\%$ . Feuerecker et al. (1993) published the correlation

$$\rho = \frac{\rho'(t)}{2} \left[ \exp\{1.2\xi_{\text{LiBr}}\} + \exp\left\{\xi_{\text{LiBr}}^2 \left(0.842 + 1.6414 \cdot 10^{-3} \frac{t}{^\circ\text{C}}\right)\right\} \right] \quad (26)$$

which is valid in the range  $10 \leq \xi_{\text{LiBr}} \leq 80\%$  but only at temperatures below the boiling point temperatures associated with pressures of 100 kPa. The principal advantage of the structure

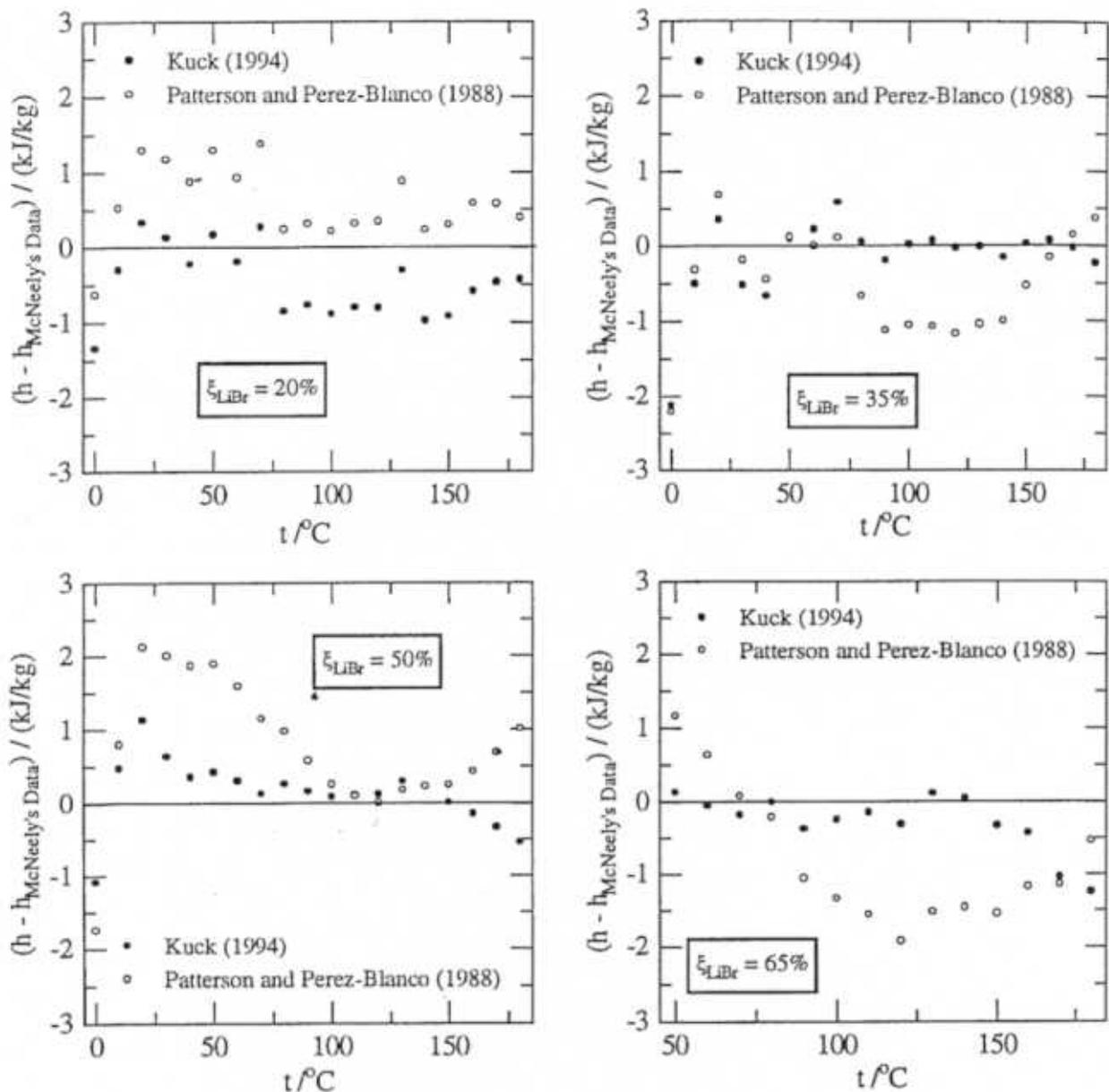


Figure 4 Enthalpy of saturated aqueous lithium bromide solution after Kuck (1994) and Patterson and Perez-Blanco (1988) compared to the data of McNeely (1979).

of this equation is that it guarantees a smooth transition to the density values of pure water  $\rho'(t)$  after Equation 2 for lithium bromide concentrations approaching zero. Figure 5 illustrates that both correlations agree well in the parameter range where both of them are valid ( $20 \leq \xi_{LiBr} \leq 65\%$ , temperatures below  $t(p = 100 \text{ kPa}, \xi_{LiBr})$ ), showing deviations of less than 2%. Feuerecker's equation yields densities up to 7% higher than those obtained by Lee's equation at temperatures above his validity range. Lee's densities at concentrations above 65% deviate from Feuerecker's values only by up to 2%, indicating that Equation 25 can be recommended even for concentrations up to 75%. The principal advantage of the structure of Equation 26 cannot compensate for its poor accuracy at high tem-

peratures. Therefore, Equation 25 was selected to be incorporated into the computer simulation code.

## PROPERTIES OF AMMONIA-WATER MIXTURE

Many studies of the thermodynamic properties of ammonia-water mixtures are cited in the literature. Results of VLE measurements have been published, among others, by Perman (1901), Wilson (1925), Wucherer (1932), Clifford and Hunter (1933), Pierre (1959), Macriss et al. (1964), Jennings (1965), Gillespie et al. (1985), Guillevic et al. (1985), Rizvi and Heide-mann (1987), and Zimmermann (1991). These experimental data were reduced by a number of authors to tables or correlations, yielding  $p$ - $t$ - $\psi$  data, as well as caloric properties. Jennings

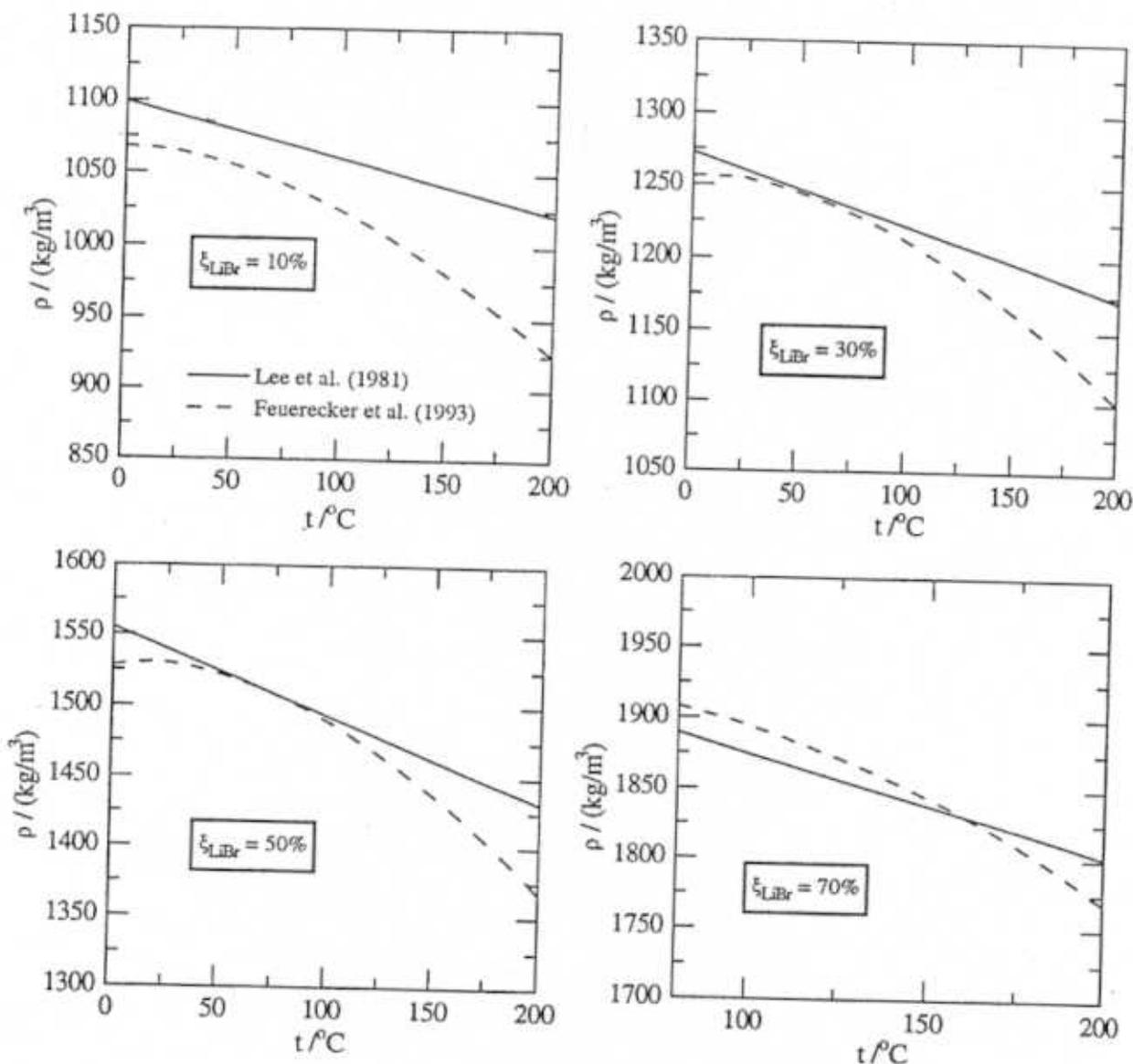
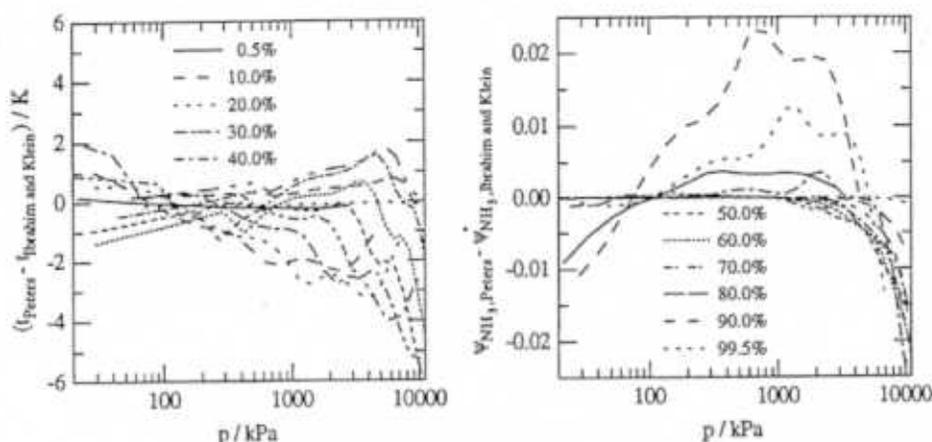


Figure 5 Density of saturated aqueous lithium bromide solution after Lee et al. (1990) and Feurecker et al. (1993).

and Shannon (1938) compiled Wucherer's data in tables, while Scatchard et al. (1947) combined Perman's and Wucherer's data in their tables. Macriss et al. (1964) extended Scatchard's tables by adding Pierre's data and their own measurements. Jennings (1981) updated his tables from 1938 by including most of the above experimental data. Jain and Gable (1971) developed polynomial equations for the boiling temperature and the vapor-ammonia concentration, both as functions of pressure and liquid ammonia concentration, and for the liquid and vapor enthalpies, based on Macriss's tables.

Schulz (1971) was the first to develop equations of state (EOS) for the Gibbs free energy of the liquid and the gaseous mixture. The two separate equations are linked by the VLE conditions of equality of the components' chemical potentials in

the liquid and in the vapor. He employed the Redlich-Kister relation for the molar excess Gibbs free energy and fitted the coefficients in the equations with most of the experimental data available to him in the range  $-73 \leq t \leq 177^\circ\text{C}$ ,  $1 \leq p \leq 2,500$  kPa. Ziegler and Trepp (1984) modified Schulz's equations and extended the validity range to  $-43 \leq t \leq 230^\circ\text{C}$ ,  $20 \leq p \leq 5,000$  kPa. Higher temperatures from  $40^\circ\text{C}$  up to  $315^\circ\text{C}$  and higher pressures from 74 kPa up to 20,000 kPa are governed by the data-reduction procedure of Gillespie et al. (1985). They employed the Redlich-Kister relation for the molar excess Gibbs free energy to calculate the activity coefficients required when solving the VLE conditions of equality of the components' partial fugacities. Zawacki and Macriss (1987) applied it for generating  $p$ - $t$ - $\psi$  tables. The procedure, however, yields only  $p$ - $t$ - $\psi$  data, but



**Figure 6** Deviations of the boiling point temperatures and the ammonia vapor concentrations of ammonia-water mixtures at VLE between the correlations of Peters (1995) and the correlations of Ibrahim and Klein (1993) at various liquid ammonia mass concentrations.

no caloric properties. The same holds true for the data-reduction procedures presented by Heidemann and Rizvi (1986) in the range  $30 \leq t \leq 345^\circ\text{C}$ ,  $30 \leq p \leq 22,000$  kPa. Ibrahim and Klein (1993) improved the equations of Ziegler and Trepp (1984) by including the experimental data of Gillespie et al. (1985) at higher temperatures and pressures, thus extending the validity range to  $-43 \leq t \leq 327^\circ\text{C}$ ,  $20 \leq p \leq 11,000$  kPa. Peters (1994) included in his VLE data reduction additional experimental data by Zimmermann (1991). His procedure provides  $p$ - $t$ - $\psi$  data in the range  $-50 \leq t \leq 230^\circ\text{C}$ ,  $10 \leq p \leq 18,000$  kPa.

The above survey of available thermodynamic properties of ammonia-water mixtures reveals that only the data-reduction procedure developed by Schulz (1971) and improved by Ziegler and Trepp (1984) and Ibrahim and Klein (1993) provides both VLE data and caloric properties in a single and self-consistent thermodynamic model. Thus, the correlations of Ibrahim and Klein (1993) were chosen to be incorporated into the computer code because they cover the widest parameter range  $-43 \leq t \leq 327^\circ\text{C}$ ,  $20 \leq p \leq 11,000$  kPa.

### Pressure-Temperature-Composition ( $p$ - $t$ - $\psi$ ) Behavior of Ammonia-Water Mixture at VLE

Ibrahim and Klein (1993) developed their correlations by employing the VLE condition that the partial fugacity of each component in the gas phase must equal its partial fugacity in the liquid mixture:

$$\phi_{\text{NH}_3}^{\text{mix}} p \psi_{\text{NH}_3} = \gamma_{\text{NH}_3} \phi_{\text{NH}_3}^{\text{pure}} p_s, \text{NH}_3 \psi_{\text{NH}_3}^{\text{pure}} \delta_{\text{NH}_3}^{\text{mix}} / \delta_{\text{NH}_3}^{\text{pure}} \quad (27)$$

$$\phi_{\text{H}_2\text{O}}^{\text{mix}} p \psi_{\text{H}_2\text{O}} = \gamma_{\text{H}_2\text{O}} \phi_{\text{H}_2\text{O}}^{\text{pure}} p_s, \text{H}_2\text{O} \psi_{\text{H}_2\text{O}}^{\text{pure}} \delta_{\text{H}_2\text{O}}^{\text{mix}} / \delta_{\text{H}_2\text{O}}^{\text{pure}} \quad (28)$$

Fitting of the experimental data yielded the fugacity coefficients  $\phi$ , the activity coefficients  $\gamma$ , and the Poynting factors  $\delta$  that are required in these equations, as functions of pressure, temperature, and concentrations. Knowing these quantities allows one, for example, to calculate from these two equations the boiling point temperature,  $t$ , and the ammonia concentra-

tion  $\psi_{\text{NH}_3}$  in the gas phase, if the pressure  $p$  and ammonia concentration  $\psi_{\text{NH}_3}$  in the liquid mixture are specified.

To assess the accuracy of the equations, they are compared with the correlations developed by Peters (1994). Peters fitted the experimental data also by means of Equations 27 and 28. But, similar to his treatment of aqueous lithium bromide solution (see the previous section), he introduced an association model that assumes an association reaction of ammonia and water molecules forming a species of clusters that is regarded as a third liquid component in the thermodynamic sense. Figure 6 shows on the left-hand side the deviation between the boiling point temperatures after the two references and, on the right-hand side, the deviation between the ammonia concentrations  $\psi_{\text{NH}_3}$  in the gas phase after the two references, as functions of the pressure for various ammonia mass concentrations in the liquid, as indicated. The chosen pressure and temperature range lies within the validity ranges of both references. The boiling point temperature deviations remain below  $\pm 2$  K at pressures below 1,000 kPa. At higher pressures the boiling point temperature after Peters assumes values up to 2 K higher and up to 6 K lower than those predicted by the correlations of Ibrahim and Klein. The maximum ammonia vapor concentration deviation is about  $\pm 0.025$  kmol/kmol, mainly at low ammonia liquid concentrations and medium pressures, and at pressures above 5,000 kPa for the whole liquid concentration range. Both references based the development of their correlations on more or less identical experimental data. Hence, the observed deviations must be attributed to the accuracy of their respective data-fitting procedures.

Equations 27 and 28 together constitute a system of nonlinear equations that has to be solved iteratively to produce the VLE properties of ammonia-water mixtures, as required in the computer code. However, any additional iteration process should be avoided in the code, as already pointed out. Therefore, Equations 27 and 28 were employed in this work to generate a base of 5,260  $p$ - $t$ - $\xi$ - $\xi$  data points in the range  $-43 \leq t \leq 327^\circ\text{C}$ ,  $20 \leq p \leq 11,000$  kPa. These numerically generated data were successfully reduced by Dühring lines of the form

TABLE 4 Numerical Values of Coefficients  $a$ ,  $b$ , and  $c$  in Equation 30

$i$	$a$	$b$	$c$
0	0.0	1.0	0.0
1	$-5.5542808 \cdot 10^{-2}$	$+2.9401340 \cdot 10^0$	$-7.3825347 \cdot 10^{-3}$
2	$+2.8903954 \cdot 10^{-3}$	$-2.9746632 \cdot 10^{-1}$	$+7.0452714 \cdot 10^{-2}$
3	$-9.9993985 \cdot 10^{-3}$	$+1.1301928 \cdot 10^{-2}$	$-2.6091336 \cdot 10^{-1}$
4	$+2.0707756 \cdot 10^{-4}$	$-2.5444689 \cdot 10^{-2}$	$+5.7941902 \cdot 10^{-1}$
5	$-2.5032344 \cdot 10^{-4}$	$+3.3726490 \cdot 10^{-2}$	$-7.7216652 \cdot 10^{-1}$
6	$+1.6201291 \cdot 10^{-4}$	$-2.3587537 \cdot 10^{-2}$	$+5.4793460 \cdot 10^{-1}$
7	$-4.3153626 \cdot 10^{-3}$	$+6.6517338 \cdot 10^{-1}$	$-1.5714291 \cdot 10^{-1}$

$$t(p, \xi_{NH_3}) = A(\xi_{NH_3}) + B(\xi_{NH_3}) \cdot t_{s, H_2O}(p) + C(\xi_{NH_3}) \cdot t_{s, H_2O}^2(p) \quad (29)$$

where  $t_{s, H_2O}$ , the saturation temperature of pure water at the pressure  $p$ , follows from Equation 1. The parameters  $A$ ,  $B$ , and  $C$  stand for the polynomials

$$\begin{aligned} A &= \sum_{i=0}^7 a_i \cdot \xi_{NH_3}^i \\ B &= \sum_{i=0}^7 b_i \cdot \xi_{NH_3}^i \\ C &= \sum_{i=0}^7 c_i \cdot \xi_{NH_3}^i \end{aligned} \quad (30)$$

with the fitted coefficients  $a_i$ ,  $b_i$ , and  $c_i$  listed in Table 4. They were calculated by minimizing the maximum absolute deviation between the boiling point temperatures that follow from Equation 29 and those of the numerically generated database in a form similar to that of Equation 10. Note that the values  $a_0 = 0$ ,  $b_0 = 1$ , and  $c_0 = 0$  were set to ensure a smooth transition to the properties of pure water for  $\xi_{NH_3}$  approaching zero.

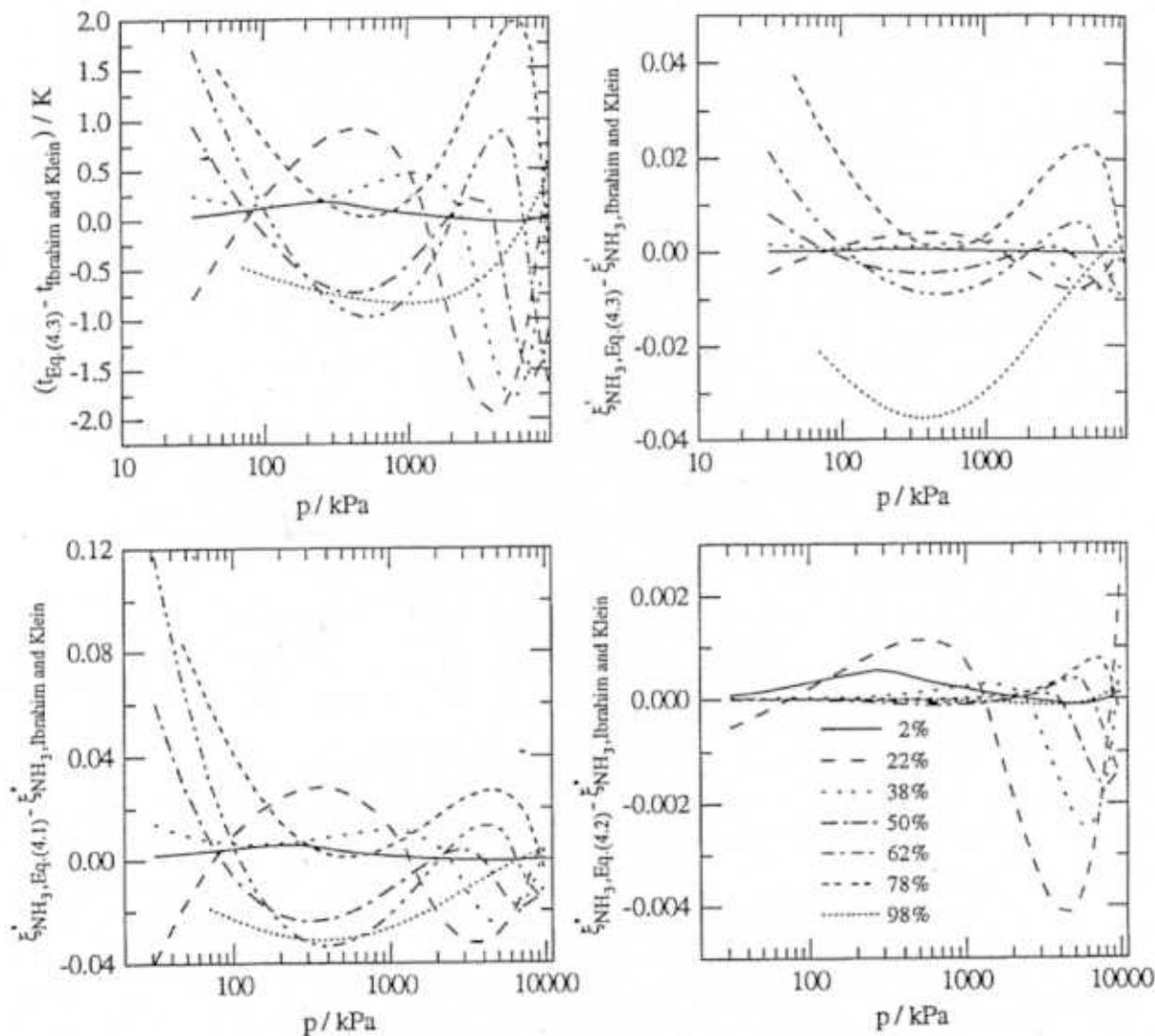
The new correlation allows one to calculate explicitly both the boiling point temperature as a function of the pressure and the saturation pressure as a function of the temperature of a liquid ammonia-water mixture of specified composition. Only the composition of the liquid mixture has to be calculated iteratively from Equation 29, in case pressure and temperature are specified. The composition of the vapor in equilibrium with the solution is provided in any case explicitly by Equation 27 or 28, when two of the three parameters—pressure, temperature, and liquid composition—are specified, and the third one is supplied by Equation 29.

Figure 7 illustrates the accuracy of this novel approach with respect to the procedure of Ibrahim and Klein (1993). It is

evident that the boiling point temperature is predicted by Equation 29 for given pressure and liquid composition with a maximum deviation of  $\pm 2$  K as compared to the results of Ibrahim and Klein. The liquid composition is predicted by Equation 29 for given pressure and temperature (corresponding to the indicated liquid composition after Ibrahim and Klein) with an accuracy of  $\pm 0.04$  kg/kg. Using the liquid composition that follows from Equation 29 for given pressure and temperature in Equations 27 and 28 produces two different vapor compositions as depicted in the lower part of Figure 7. Note that the VLE condition of equality of the partial fugacities of liquid ammonia and ammonia vapor (Equation 27) predicts the vapor composition for given pressure and temperature with a maximum deviation of  $-0.04$  kg/kg to  $+0.12$  kg/kg, as opposed to the VLE condition of equality of the partial fugacities of liquid water and water vapor (Equation 28), which predicts the vapor composition far more accurately with a maximum deviation of only  $-0.004$  kg/kg to  $+0.002$  kg/kg. Thus, Equation 28 was selected for calculation of the vapor composition in the computer code. The observed deviations compare well with the accuracy of the procedure of Ibrahim and Klein itself with respect to the model of Peters (1994), as illustrated in Figure 6. The advantage of Equation 29, namely its explicitness in the boiling temperature and in the saturation pressure, compensates for the insignificant loss in accuracy.

### Caloric Properties of Ammonia-Water Mixture

Caloric properties of liquid and gaseous ammonia-water mixtures can be obtained for both superheated and subcooled or saturated states from the equations of state for the molar Gibbs free energy that were developed in the first place by Schulz (1971). The two separate equations for the liquid and the vapor have the structure



**Figure 7** Deviations of the boiling point temperatures and the ammonia concentrations of liquid and vapor of ammonia-water mixtures at VLE between the correlations developed in this work and the correlations of Ibrahim and Klein (1993) at various temperatures that correspond to the indicated liquid ammonia mass concentrations after Ibrahim and Klein.

$$\begin{aligned}
 g^m(p, T, \psi) = & \psi_{\text{NH}_3} g_{\text{NH}_3}^{m, \text{pure}}(p, T) \\
 & + \psi_{\text{H}_2\text{O}} g_{\text{H}_2\text{O}}^{m, \text{pure}}(p, T) \\
 & + \Delta g_{\text{mix}}^m(T, \psi) + \Delta g^m(p, T, \psi)
 \end{aligned} \quad (31)$$

with the molar Gibbs free energy of mixing

$$\Delta g_{\text{mix}}^m(T, \psi) = RT(\psi_{\text{NH}_3} \ln \psi_{\text{NH}_3} + \psi_{\text{H}_2\text{O}} \ln \psi_{\text{H}_2\text{O}}). \quad (32)$$

Assuming ideal vapor mixtures, the molar excess Gibbs free energy  $\Delta g_{\text{mix}}^{m, \text{vapor}}$  of the vapor is set to zero. The molar excess Gibbs free energy of the liquid is given by the Redlich-Kister relation:

$$\begin{aligned}
 \Delta g^m(p, T, \psi) = & \psi_{\text{NH}_3} \psi_{\text{H}_2\text{O}} [D_1(p, T) \\
 & + D_2(p, T)(\psi_{\text{NH}_3} - \psi_{\text{H}_2\text{O}}) \\
 & + D_3(p, T)(\psi_{\text{NH}_3} - \psi_{\text{H}_2\text{O}})^2]
 \end{aligned} \quad (33)$$

where the pressure and temperature-dependent  $D_i$  are expressed by algebraic functions containing 16 coefficients altogether that were fitted by Ibrahim and Klein (1993). In their data-fitting procedure they made use of algebraic expressions for the Gibbs free energies of the pure components ammonia and water as functions of pressure and temperature as published by Ziegler and Trepp (1984). After substituting these expressions and Equations 32 and 33 into Equation 31, all caloric properties of the mixture can be obtained as explicit

functions of pressure, temperature, and composition by simple mathematical manipulations. Molar volume, molar enthalpy, and molar entropy follow from

$$v^m(p, T, \psi) = \left( \frac{\partial g^m}{\partial p} \right)_{T, \psi} \quad (34)$$

$$h^m(p, T, \psi) = -T^2 \left( \frac{\partial (g^m/T)}{\partial T} \right)_{p, \psi} \quad (35)$$

and

$$s^m(p, T, \psi) = - \left( \frac{\partial g^m}{\partial T} \right)_{p, \psi} \quad (36)$$

for subcooled liquid, superheated vapor, and both liquid and gaseous mixtures in VLE.

## CONCLUSION

Various published equations describing the thermodynamic properties of liquid water, water vapor, aqueous lithium bromide solution, and ammonia-water mixtures have been studied with respect to three major criteria:

- One particular fluid property should be described by only a single equation within the whole desired parameter range.
- The transition from one property equation to another, if necessary after all, should be smooth.
- All equations should be explicit in the property in question.

By correlating data published by Peters and Keller (1994), a novel equation for the boiling point temperature of LiBr-H<sub>2</sub>O solution has been developed that covers the concentration range from 0% to 76% LiBr. VLE data of Ibrahim and Klein (1993) were used for developing a novel correlation for the boiling point temperature of ammonia-water mixtures. Equations meeting the above requirements have been implemented in the computer code for simulation of absorption heat pump cycles, providing it with an improved and updated property database that is consistent and extremely robust.

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## NOMENCLATURE

- $c_{p,v}$  = specific heat of superheated water vapor (kJ/kg·K)  
 $g$  = Gibbs free energy (kJ/kg [kJ/kmol])  
 $h$  = specific enthalpy (kJ/kg [kJ/kmol])  
 $K_C$  = equilibrium constant of dissociation reactions producing Li<sup>+</sup> and Br<sup>-</sup> ions coated with H<sub>2</sub>O molecules (-)  
 $m$  = solvation number of dissociation reactions producing Li<sup>+</sup> and Br<sup>-</sup> ions coated with H<sub>2</sub>O molecules (-)  
 $p$  = pressure (kPa)  
 $R$  = universal gas constant (8.315 kJ/[kmol·K])

- $s$  = specific entropy (kJ/kg·K [kJ/kmol·K])  
 $t, T$  = temperature (°C [K])  
 $v$  = specific volume (m<sup>3</sup>/kg [m<sup>3</sup>/kmol])

## Greek

- $\gamma$  = activity coefficient (-)  
 $\delta$  = Poynting factor (-)  
 $\theta$  = normalized temperature (=  $T/T_c$ )  
 $\xi$  = mass concentration (kg component/kg mixture)  
 $\rho$  = density (kg/m<sup>3</sup>)  
 $\tau$  = normalized temperature (=  $1 - T/T_c$ )  
 $\phi$  = fugacity coefficient (-)  
 $\psi$  = mole concentration (kmol component/kmol mixture)

## Subscripts

- $c$  = critical point  
 $C$  = cluster as component in solution after dissociation of LiBr  
 $H$  = water as component in solution after dissociation of LiBr  
 $i$  = index for component in a mixture  
 $L$  = lithium bromide as component in solution after dissociation of LiBr  
 $LiBr$  = lithium bromide as component in solution before dissociation  
 $s$  = saturated

## Superscripts

- $m$  = molar property  
 $'$  = saturated liquid  
 $''$  = saturated vapor

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#### QUESTIONS AND COMMENTS

**S.A. Klein, Professor, University of Wisconsin, Madison:** Why did you use tenth-order polynomials for the LiBr-H<sub>2</sub>O correlations?

**Hans-Martin Hellmann:** We increased the order of the polynomials until the gain in accuracy became insignificant.

**Keith Herold, Department of Mechanical Engineering, University of Maryland, College Park:** I would like to bring your attention to a work published previously in the *ASHRAE Transactions* that you do not cite in your paper. This work deals with the properties of LiBr/H<sub>2</sub>O and appears to be directly relevant to a major part of your study:

Herold, K.E., and M.J. Moran, 1987. A Gibbs free energy expression for calculating thermodynamic properties of lithium bromide/water solutions. *ASHRAE Transactions* 93(1): 35-48.

**Hellmann:** In the recent literature studied in this work, unfortunately no reference was made to your work. Thus, we have not been familiar with it while conducting our study. I am sure that it would probably have been very useful to us.