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Enthalpy Changes upon Partial Evaporation of Aqueous Solutions Containing Ammonia and Carbon Dioxide†

Bernd Rumpf, Frank Weyrich, and Gerd Maurer*

Lehrstuhl für Technische Thermodynamik, Universität Kaiserslautern, D-67653 Kaiserslautern, Germany

The enthalpy changes upon partial evaporation of aqueous solutions containing ammonia and of aqueous solutions containing ammonia and carbon dioxide were measured at temperatures from 313 to 393 K with a thin film evaporator flow calorimeter. The molalities of ammonia and carbon dioxide entering the calorimeter ranged up to 12 and 6 mol/kg, respectively. The physicochemical model originally developed by Edwards et al. (1978) and further modified and extended by Kurz et al. (1995) to describe phase equilibria in aqueous systems containing ammonia and carbon dioxide is used to derive a predictive enthalpy model for this complex, chemical reactive system. Comparisons between the new experimental results for the enthalpy change upon partial evaporation and model predictions reveal deviations mostly within the experimental uncertainties.

Introduction

The thermodynamic properties of aqueous solutions containing ammonia and sour gases such as carbon dioxide, sulfur dioxide, or hydrogen sulfide must be known in many applications. Typical examples are the cleaning of raw gases in power stations, the production of fertilizers, or applications in the field of environmental protection. The design of such processes requires information on the thermodynamic properties of the mixtures, among those primarily phase equilibria, caloric properties, and often also information on the kinetics of mass transfer and chemical reactions. Due to chemical reactions in the liquid phase and a strong deviation from ideality, aqueous solutions containing the weak base ammonia and sour gases such as carbon dioxide are characterized by a complex thermodynamic behavior. Although experimental information on phase equilibria, especially in the system $NH_3-CO_2-H_2O$, is now available over a considerable range of temperature and composition (Göppert and Maurer, 1988; Müller et al., 1988; Kurz et al., 1995), very little is known about the caloric properties. The model originally developed by Edwards et al. (1978) and further extended and modified by Kurz et al. (1995) is used to derive a predictive enthalpy model for those solutions. However, no experimental information is available to test the model predictions. Therefore, the enthalpy change upon partial evaporation of aqueous solutions containing ammonia and of aqueous solutions containing ammonia and carbon dioxide simultaneously was measured with a thin film evaporator flow calorimeter over a wide range of temperature and composition. Experimental results are reported and compared with model predictions.

Experimental Section

Experimental Equipment and Procedure. Figure 1 shows a simplified scheme of the equipment to measure the enthalpy change upon partial evaporation of liquid mixtures. The equipment is a modification of an apparatus previously used by Liu and Maurer (1992) and Liu et al. (1992) to determine the enthalpy change upon partial evaporation of aqueous and methanolic formaldehyde solutions. The apparatus and procedure have been described in detail (Weyrich, 1997), therefore only a brief outline is given here.

A high precision diaphragm pump (d; Lewa, Leonberg, Germany) pumps the liquid solution from a pressurized supply tank (b) through a heat exchanger tube (e; length ∼18 m) into the calorimeter (f), which is placed in a thermostat. In that calorimeter, a rotating coil spreads the liquid mixture on the inner surface of a thin-walled tube. Power supplied by an electrical heater soldered on the outer surface of that tube causes the liquid mixture to partially vaporize. The resulting phases are separated inside the calorimeter. The vapor phase leaves the calorimeter through a heated line (h), and the liquid phase leaves through a siphon (i). During an experiment, the vapor and liquid phases are collected in separate weighing condensors (j and l) that are cooled by liquid nitrogen or a mixture of solid carbon dioxide and ethanol. Before and after an experiment, the liquid and vapor phase are collected in a single condensor (k). The condensors are also used to transfer the pressure from the helium-filled pressure regulator system to the calorimeter.

The solutions (typically ∼1 kg) are prepared in an evacuated tank (a). The masses of water, ammonia, and carbon dioxide are determined by weighing with an uncertainty of about ±0.08 g. After preparing the solution, the tank is pressurized to a pressure well above the boiling point pressure of the solution to avoid the presence of a gas phase. After thorough mixing, the solution is filled into two thermostated, pressurized supply tanks (b) that are used alternately. Pressure is supplied to the solution through a piston sealed with Teflon rings that separates the liquid from compressed nitrogen (PL). The supply tanks, the heat exchanger tube, and the calorimeter are thermostated with two thermostats (c) to the same temperature.

A constant pressure is achieved by a pressure regulator system (t; MKS, Andover, MA) in connection with a

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* To whom correspondence should be addressed. Phone: +49 631 205 2410. Fax: +49 631 205 3835. E-mail: gmaurer@rhrk.uni-kl.de.

† Dedicated to Prof. John M. Prausnitz on the occasion of his 70th birthday.

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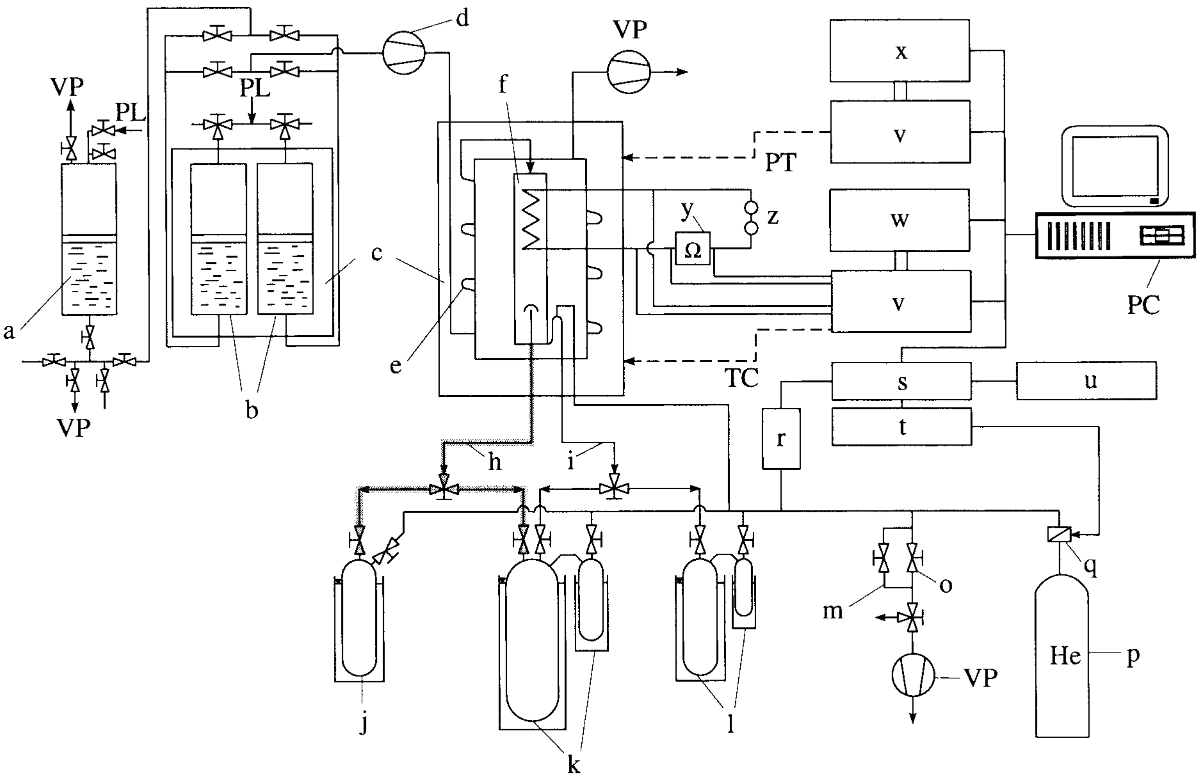

Figure 1. Simplified scheme of the experimental equipment to measure the enthalpy change upon partial evaporation of liquid mixtures: a, pressurized tank for preparing the solutions; b, pressurized supply tanks; c, thermostats; d, precision diaphragm pump; e, heat exchanger; f, calorimeter; h, heated line for collecting the vapor phase; i, line for collecting the liquid phase; j, weighing condensor for vapor phase; k, main condensor for liquid and vapor; l, weighing condensor for liquid phase; m, bypass; o, throttle valve; p, gas storage; q, magnetic valve; r, precision pressure transducer; s, pressure reading; t, pressure regulator; u, plotter; v, multiway switch; w, high precision multimeter; x, high precision automatic bridge; y, precision resistor; z, constant potential difference power supply; PC, personal computer; PT, platinum resistance thermometers; PL, connectors for pressurizing the solutions; TC, thermocouples; VP, vacuum pumps.

magnetic valve (q). The pressure is measured with three pressure transducers (r; WIKA GmbH, Klingenberg, Germany) with ranges 0−0.25, 0−0.6, and 0−2.5 MPa. Before and after each series of measurements, the transducers are calibrated with a high-precision pressure gauge (Desgranges & Huot, Aubervilliers, France). The uncertainties in determining the total pressure are 0.35 kPa in the range 0−0.25 MPa, 0.55 kPa in the range 0.25−0.6 MPa, and 3.5 kPa at pressures >0.6 MPa.

The temperature of the liquid entering as well as that of the coexisting liquid and vapor phases leaving the calorimeter are determined by calibrated platinum resistance thermometers (PT) in connection with a high-precision resistance bridge (AΣL F26; Milton Keynes, U.K.). The uncertainty in the temperature measurement is less than ±0.1 K. Furthermore, the temperature profile along the calorimeter tube is measured by several thermocouples (TC).

The electrical power supplied to the calorimeter is provided by a high-precision constant voltage power supply (z; Rohde & Schwarz, Munich, Germany). The electrical energy is determined from the electrical power supplied to the calorimeter and the time for the experiment (typically ∼1200−2700 s), which was determined with an uncertainty of ±0.2 s. The electrical power is determined from the potential difference across the heater and the electric current. The latter is determined by measuring the potential difference across a high precision standard resistor (y; Burster GmbH, Gernsbach, Germany) with a precision digital voltmeter (w; Prema, Mainz, Germany). The relative uncertainty in determining the electrical power supplied to the calorimeter tube is less than ±0.04%.

The masses of the liquid and gaseous phases are determined by weighing the condensors before and after an experiment. The typical masses of the vapor- and liquid-phase samples were ∼3 and ∼70 g, respectively. Two balances (type PM 1200 and PM 4000, Mettler, Giessen, Germany) are used to determine the sample masses. Corrections for the masses of helium in the weighing condensors are applied (for details see Weyrich, 1997). The uncertainties in the masses of the vapor and liquid-phase samples are <0.08 and 0.2 g, respectively (for details see also Tables 5, 6, and 8). The overall molalities of ammonia and carbon dioxide in the liquid phase leaving the calorimeter are determined by titration with uncertainties of <1.5% (for details see Weyrich, 1997).

The enthalpy change upon partial evaporation is calculated by applying the first law of thermodynamics to the calorimeter:

$$Q_{\mathrm{el}} + Q_{\mathrm{loss}} + W = \Delta H + \Delta E_{\mathrm{kin}} + \Delta E_{\mathrm{pot}} \qquad (1)$$

where Q_{el} and Q_{loss} are the electrical energy supplied to the calorimeter and the heat loss to or from the surroundings, respectively. The calorimeter tube was surrounded by a thermostated vacuum jacket evacuated to $<10^{-3}$ Pa (for a detailed description of the calorimeter see Weyrich, 1997). To minimize the heat loss due to radiation, two radiation shields were mounted in the vacuum jacket. A detailed calculation showed that the heat loss due to radiation can be neglected compared

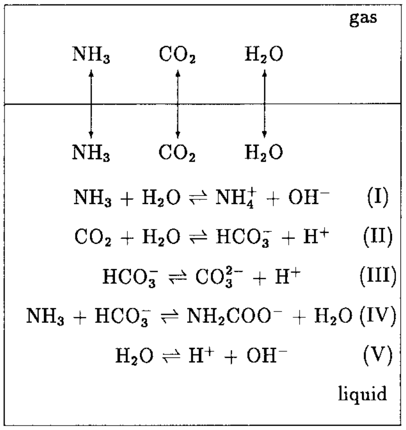

Figure 2. VLE and chemical reactions in the ammonia−carbon dioxide−water system.

with the electrical energy supplied to the calorimeter tube. Another source of heat loss is heat conduction at the lower end of the calorimeter tube where heat is conducted from the calorimeter tube to the surroundings; that is, to the vapor and liquid phase sampling lines. As discussed by Weyrich (1997), that contribution can also be neglected.

The decrease in the specific potential energy of the samples (due to the different positions of the entrance and exit of the calorimeter) is <0.005 J/g, the increase in the specific kinetic energy is <0.015 J/g (see Weyrich, 1997). As those two effects at least partially compensate each other and the measured enthalpy changes are typically of the order of 2 kJ/g of vapor phase, the changes in the potential and kinetic energies are neglected. A detailed investigation of Liu and Maurer (1992) also showed that the mechanical work W supplied by the rotating coil can be neglected. Therefore, the enthalpy change upon partial evaporation is directly calculated from the measured electrical energy:

$$\Delta H = Q_{\mathrm{el}} \qquad (2)$$

Substances

Carbon dioxide (≥99.995 mol %) and ammonia (≥99.999 mol %) were purchased from Messer-Griesheim, Ludwigshafen, Germany, and used without further purification. Deionized water was further purified by vacuum distillation.

Modeling

Vapor−Liquid Equilibrium Model. The model to describe vapor−liquid and vapor−liquid−solid equilibria in the system NH_3−CO_2−H_2O has been described in detail by Kurz et al. (1995), therefore only a short overview is given here. Figure 2 shows a scheme of that model. Due to chemical reactions in the liquid phase, ammonia and carbon dioxide are not only present in neutral but also in ionic form. Five chemical reactions are considered in the liquid phase: the protolysis of ammonia and carbon dioxide, the dissociation of bicarbonate, the formation of carbamate and the autoprotolysis of water. The condition for chemical equilibrium in the liquid phase is expressed by the chemical reaction equilibrium constant K_R. The influence of pressure on K_R is neglected:

$$K_{\mathrm{R}}(T) = \prod_i a_i^{\nu_{i,\mathrm{R}}} \qquad \mathrm{R} = \mathrm{I}\ldots\mathrm{V} \qquad (3)$$

where a_i is the activity of component i and $\nu_{i,\mathrm{R}}$ is the stoichiometric number of component i in reaction R ($\nu_{i,\mathrm{R}} > 0$ for reaction products and $\nu_{i,\mathrm{R}} < 0$ for reaction educts). Activities are calculated applying an unsymmetrical normalization. The reference state of a dissolved species i is chosen as the hypothetical infinite diluted component in water; that is:

$$\mu_i = \mu_i(T, p, m_i \rightarrow m^{\ominus}(\mathrm{conc.}), m_i \rightarrow 0 \text{ in water (interactions)}) + RT \ln a_i \qquad i \neq w \quad (4)$$

For water, the reference state is the pure solvent at T and p of the solution

$$\mu_{\mathrm{w}} = \mu_{\mathrm{w}}(T,p)_{\mathrm{pure}} + RT \ln a_{\mathrm{w}} \qquad (5)$$

Together with the balance equation for the true number of moles of species i

$$n_{i,\mathrm{liq}} = \bar{n}_{i,\mathrm{liq}} + \sum_{\mathrm{R}} \nu_{i,\mathrm{R}} \xi_{\mathrm{R}} \qquad \mathrm{R} = \mathrm{I}\ldots\mathrm{V} \qquad (6)$$

where $\bar{n}_{i,\mathrm{liq}}$ is the overall number of moles of component i in the liquid phase (i.e., $\bar{n}_{i,\mathrm{liq}} = \bar{m}_i \times 1$ kg for $i = NH_3$, CO_2, H_2O, and $\bar{n}_{i,\mathrm{liq}} = 0$ for all other species) and ξ_{R} is the extent of reaction R, the condition for chemical equilibrium is used to calculate the true composition of the liquid phase from given overall molalities of ammonia and carbon dioxide at a given temperature. The total pressure and the composition of the vapor phase are calculated from extended Raoult's law for water

$$p y_{\mathrm{w}} \varphi_{\mathrm{w,gas}} = p_{\mathrm{w}}^{\mathrm{s}} \varphi_{\mathrm{w}}^{\mathrm{s}} \exp\left(\frac{v_{\mathrm{w}}^{\mathrm{s}}(p - p_{\mathrm{w}}^{\mathrm{s}})}{RT}\right) a_{\mathrm{w}} \qquad (7)$$

and extended Henry's law for solutes NH_3 and CO_2:

$$p y_i \varphi_{i,\mathrm{gas}} = H_{i,\mathrm{w}}^{(\mathrm{m})}(T,p_{\mathrm{w}}^{\mathrm{s}}) \exp\left(\frac{v_{i,\mathrm{w}}^{\infty}(p - p_{\mathrm{w}}^{\mathrm{s}})}{RT}\right) m_i \gamma_i^* \qquad i = NH_3, CO_2 \quad (8)$$

The calculation of the phase equilibrium requires the knowledge of the five temperature-dependent equilibrium constants K_R, the activity coefficients of all species present in the liquid phase, Henry's constants $H_{i,\mathrm{w}}^{(\mathrm{m})}$ for ammonia and carbon dioxide in pure water, the vapor pressure $p_{\mathrm{w}}^{\mathrm{s}}$, and molar volume of water $v_{\mathrm{w}}^{\mathrm{s}}$, as well as information on the vapor phase nonideality ($\varphi_{i,\mathrm{gas}}$) and the partial molar volumes $v_{i,\mathrm{w}}^{\infty}$ of ammonia and carbon dioxide at infinite dilution in water. The equilibrium constants K_{I} to K_{V} are taken from Bieling et al. (1989; see Table 1). Henry's constants for ammonia and carbon dioxide are taken from Bieling et al. (1989) and Rumpf and Maurer (1993), respectively (see Table 2). The vapor pressure $p_{\mathrm{w}}^{\mathrm{s}}$ and the molar volume of water $v_{\mathrm{w}}^{\mathrm{s}}$ are taken from Saul and Wagner (1987). A truncated virial equation of state is used to calculate the fugacity coefficients φ_i. Pure component second virial coefficients $B_{i,i}$ are calculated from a correlation based on the data recommended by Dymond and Smith (1980; see Table 3). The mixed second virial coefficients $B_{i,j}$ are taken from Hayden and O'Connell (1975). The partial molar volumes of ammonia and carbon dioxide at infinite

Table 1. Equilibrium Constants for Chemical Reactions I−V[a]

$$\ln K_R = \frac{A_R}{(T/K)} + B_R \ln(T/K) + C_R(T/K) + D_R$$

reaction	A_R	B_R	$C_R \times 10^2$	D_R
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	−5930.7	−15.063	−1.1127	97.976
$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$	−7742.6	−14.506	−2.8104	102.28
$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$	−8982.0	−18.112	−2.2249	116.73
$NH_3 + HCO_3^- \rightleftharpoons NH_2COO^- + H_2O$	552.69	−4.0400	0.46898	19.817
$H_2O \rightleftharpoons H^+ + OH^-$	−13445.9	−22.4773	0	140.932

[a] From Edwards et al., 1978; and Bieling et al., 1989.

Table 2. Henry's Constant for the Solubility of Ammonia and Carbon Dioxide in Pure Water (273 ≤ *T*/K ≤ 473)[a]

$$\ln H_{i,w}^{(m)}(T,p_w^s)/(\mathrm{MPa\cdot kg\cdot mol^{-1}}) = A_{i,w} + \frac{B_{i,w}}{(T/K)} + C_{i,w}(T/K) + D_{i,w}\ln(T/K) + \frac{E_{i,w}}{(T/K)^2}$$

i	$A_{i,w}$	$B_{i,w}$	$C_{i,w}$	$D_{i,w}$	$E_{i,w}$
NH_3	3.932	−1879.02			−355134.1
CO_2	192.876	−9624.4	0.01441	−28.749	

[a] From Bieling et al., 1989; and Rumpf and Maurer, 1993.

Table 3. Pure Component Second Virial Coefficients (273 ≤ *T*/K ≤ 473)

$$B_{i,i}/(\mathrm{cm^3/mol}) = a_{i,i} + b_{i,i}\left(\frac{c_{i,i}}{(T/K)}\right)^{d_{i,i}}$$

i	$a_{i,i}$	$b_{i,i}$	$c_{i,i}$	$d_{i,i}$
NH_3	4.059	−117.713	405.6	2.5
CO_2	65.703	−184.854	304.16	1.4
H_2O	−53.53	−39.29	647.3	4.3

Table 4. Interaction Parameters To Describe VLE and SLE in the Ammonia−Carbon Dioxide−Water System (313 ≤ *T*/K ≤ 473)[a]

$$f(T) = q_0 + \frac{q_1}{T/K} + q_2(T/K)$$

parameter	q_0	q_1	q_2
$\beta^{(0)}_{NH_3,NH_3}$	−0.0197	9.864	
τ_{NH_3,NH_3,NH_3}	5.539×10^{-3}	−0.1789	-8.61×10^{-4}
$\beta^{(0)}_{NH_3,HCO_3^-}$	0.2857	−99.466	
$\beta^{(0)}_{NH_3,CO_3^{2-}}$	−0.3391	151.28	
$\beta^{(0)}_{NH_3,NH_2COO^-}$	−0.03933	25.263	
$\beta^{(0)}_{CO_2,HCO_3^-}$	0.0843	−16.148	
$\beta^{(0)}_{NH_4^+,HCO_3^-}$	0.1134	−45.679	
$\beta^{(0)}_{NH_4^+,CO_3^{2-}}$	−0.146		
$\tau_{CO_2,NH_4^+,HCO_3^-}$	-1.1264×10^{-3}		
$\tau_{NH_4^+,NH_4^+,HCO_3^-}$	5.0715×10^{-4}		
$\tau_{NH_4^+,NH_4^+,CO_3^{2-}}$	1.4007×10^{-2}		

[a] From Rumpf et al., 1997; and Kurz et al., 1995.

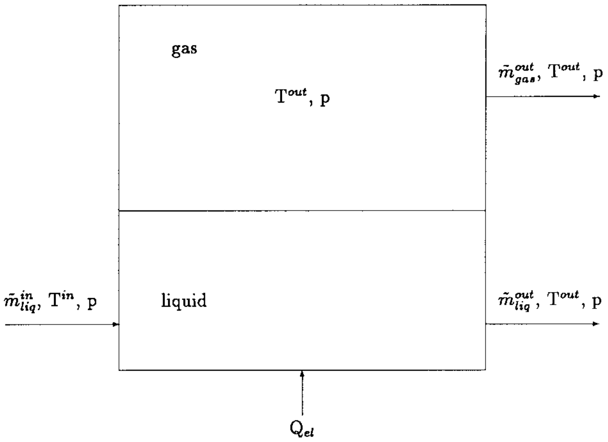

Figure 3. Scheme demonstrating the partial evaporation of a mixture.

dilution in water are calculated as recommended by Brelvi and O'Connell (1972). Activity coefficients are calculated from the Pitzer (1973) model for the excess Gibbs energy of an aqueous electrolyte solution (see, for example, Bieling et al. (1995)). Interaction parameters for the system NH_3-H_2O are taken from Rumpf et al. (1997), and those for $NH_3-CO_2-H_2O$ are from Kurz et al. (1995; see Table 4). The calculation furthermore requires the dielectric constant of pure water, which is taken from Bradley and Pitzer (1979).

Enthalpy Model. Figure 3 shows a scheme demonstrating the partial evaporation in the calorimeter. A subcooled liquid stream entering the calorimeter with the temperature T^{in} is partially evaporated at a constant pressure p. The resulting gaseous and liquid streams leave the calorimeter with the temperature T^{out}. The quantity of heat necessary for that isobaric process is calculated from the first law of thermodynamics (i.e., eq 2). The enthalpy change is expressed as

$$\Delta H = H^{out} - H^{in} = \sum_i n_{i,liq}^{out} h_{i,liq}^{out} + \sum_{i = NH_3,CO_2,H_2O} n_{i,gas}^{out} h_{i,gas}^{out} - \sum_i n_{i,liq}^{in} h_{i,liq}^{in} \quad (9)$$

where the first two terms describe the enthalpy of the liquid and gaseous streams leaving the calorimeter and the last term is the enthalpy of the subcooled liquid entering the calorimeter. Only the volatile components water, carbon dioxide, and ammonia are vaporized, so the balance equation for the overall number of moles $\bar{n}_{i,liq}$ of those components in the liquid phase is

$$\bar{n}_{i,liq}^{out} = \bar{n}_{i,liq}^{in} - n_{i,gas}^{out} \qquad i = NH_3, CO_2, H_2O \quad (10)$$

Combining eqs 6 and 10 gives

$$n_{i,liq}^{out} - n_{i,liq}^{in} = \sum_R \nu_{i,R}(\xi_R^{out} - \xi_R^{in}) - n_{i,gas}^{out} \quad (11)$$

Inserting eq 11 into eq 9 results in the following equation for the enthalpy change upon partial evaporation

$$\Delta H = \sum_i n_{i,\text{liq}}^{\text{in}}(h_{i,\text{liq}}^{\text{out}} - h_{i,\text{liq}}^{\text{in}}) + \sum_{\text{R}} \Delta\xi_{\text{R}} \Delta_{\text{R}} h_{\text{liq}}^{\text{out}} + \sum_i n_{i,\text{gas}}^{\text{out}}(h_{i,\text{gas}}^{\text{out}} - h_{i,\text{liq}}^{\text{out}}) \quad (12)$$

where $\Delta\xi_{\text{R}} = \xi_{\text{R}}^{\text{out}} - \xi_{\text{R}}^{\text{in}}$ is the change of the extent of a chemical reaction R and $\Delta_{\text{R}}h_{\text{liq}}$ is the reaction enthalpy for a chemical reaction R in the liquid phase:

$$\Delta_{\text{R}} h_{\text{liq}} = \sum_i \nu_{i,\text{R}} h_i(T,p,m_j) \quad (13)$$

Equation 12 reveals that the enthalpy change upon evaporating a chemical reactive mixture can be split up into three effects: The first term in eq 12 is the enthalpy change for heating the subcooled liquid mixture from temperature T^{in} to temperature T^{out}, the second term results from the change in the extent of the chemical reactions at temperature T^{out}, and the last term describes the enthalpy change due to the mass transfer from the liquid into the vapor at temperature T^{out}. Equation 12 may be further examined by splitting up the partial molar enthalpies h_i into reference state enthalpies $h_{i,\text{liq}}^{\text{ref}}$ and excess enthalpies h_i^{E}: For a component i in the liquid phase, the enthalpy is

$$h_{i,\text{liq}} = h_{i,\text{liq}}^{\text{ref}} + h_i^{\text{E}} \quad (14)$$

As for a solute i, the reference state is the hypothetical infinite diluted component in water at unit molality, the reference state enthalpy of a solute i is

$$h_{i,\text{liq}}^{\text{ref}} = h_i(T,\ p,\ m_i \rightarrow m^{\ominus}(\text{concentration}),\ m_i \rightarrow 0 \text{ in water (interactions)}) \quad (15)$$

$$= h_{i,\text{w}}^{\infty}(T,p)$$

For water, the reference state is the pure solvent at T and p of the solution:

$$h_{\text{w,liq}}^{\text{ref}} = h_{\text{w}}(T,p)_{\text{pure}} \quad (16)$$

For a gaseous component, the reference state is the pure component at pressure p and temperature T in the ideal gas state. Thus, the enthalpy of a gaseous component is

$$h_{i,\text{gas}}(T,p,y_j) = h_{i,\text{id.gas}}(T) + \delta h_{i,\text{gas}}(T,p,y_j) \quad (17)$$

where $\delta h_{i,\text{gas}}$ is the residual part of the partial molar enthalpy. Neglecting the (small) pressure dependence of the partial molar enthalpies in the reference state and introducing eq 14 into eq 12 finally results in the following expression for the enthalpy change upon partial evaporation:

$$\begin{aligned}\Delta H = {} & \sum_i n_{i,\text{liq}}^{\text{in}}(h_{i,\text{liq}}^{\text{Ref}}(T^{\text{out}}) - h_{i,\text{liq}}^{\text{Ref}}(T^{\text{in}})) + \\ & \sum_i n_{i,\text{liq}}^{\text{in}}(h_{i,\text{liq}}^{\text{E}}(T^{\text{out}},p,m_j^{\text{out}}) - h_{i,\text{liq}}^{\text{E}}(T^{\text{in}},p,m_j^{\text{in}})) + \\ & \sum_{\text{R}} \Delta\xi_{\text{R}}\Delta_{\text{R}} h_{\text{liq}}^{\text{Ref}}(T^{\text{out}}) + \sum_i n_{i,\text{gas}}^{\text{out}}(h_{i,\text{gas}}(T^{\text{out}},p,y_j) - \\ & h_{i,\text{liq}}(T^{\text{out}},p,m_j^{\text{out}})) + \sum_{\text{R}} \Delta\xi_{\text{R}}\Delta_{\text{R}} h_{\text{liq}}^{\text{E}}(T^{\text{out}},p,m_j^{\text{out}}) \quad (18)\end{aligned}$$

where

$$\Delta_{\text{R}} h_{\text{liq}}^{\text{E}} = \sum_i \nu_{i,\text{R}} h_i^{\text{E}}(T,p,m_j) \quad (19)$$

The first term in eq 18 may be interpreted as the enthalpy change upon heating the components of the liquid mixture in their reference states from T^{in} to T^{out}. The third term is the enthalpy change resulting from a change in the extent of the chemical reactions at temperature T^{out} in the reference state. The fourth term is the enthalpy change due to the vaporization of the volatile components at temperature T^{out}. The second and fifth term in eq 18 describe effects due to the nonideality of the liquid solution. The calculation requires the temperature-dependent partial molar enthalpies of all species in the liquid phase as well as the partial molar enthalpies of the gaseous species. The excess enthalpy of a species i in the liquid phase can be expressed by the change of the activity with temperature:

$$h_i^{\text{E}}(T,p,m_j) = -RT^2\left(\frac{\partial \ln a_i}{\partial T}\right)_{p,m_j} \quad (20)$$

For a gaseous component, the residual part $\delta h_{i,\text{gas}}$ of the partial molar enthalpy is

$$\delta h_{i,\text{gas}}(T,p,y_j) = -RT^2\left(\frac{\partial \ln \varphi_{i,\text{gas}}}{\partial T}\right)_{p,y_j} \qquad i = \text{NH}_3,\ \text{CO}_2,\ \text{H}_2\text{O} \quad (21)$$

Details of the calculation of those properties from the equilibrium model are given in the *Appendix*.

Evaluation of the Experimental Results. The enthalpy change upon partial evaporation is calculated from the experimental results for the temperatures T^{in} and T^{out}, the masses of the vapor and liquid phases $\tilde{m}_{\text{gas}}$ and $\tilde{m}_{\text{liq}}$ leaving the calorimeter, and the overall molalities of ammonia $\bar{m}_{\text{NH}_3}^{\text{in}}$ and carbon dioxide $\bar{m}_{\text{CO}_2}^{\text{in}}$ entering the calorimeter by performing the following steps:

1. First, the extents of all reactions and the true composition of the subcooled liquid stream entering the calorimeter are calculated from the experimental results for the temperature T^{in} and the overall molalities $\bar{m}_{\text{CO}_2}^{\text{in}}$ and $\bar{m}_{\text{NH}_3}^{\text{in}}$ by applying eqs 3 and 6.

2. Second, the overall number of moles of ammonia, carbon dioxide, and water ($\bar{n}_{i,\text{liq}}^{\text{in}}$, $i = \text{NH}_3, \text{CO}_2, \text{H}_2\text{O}$) entering the calorimeter are calculated from the overall molalities of ammonia and carbon dioxide ($\bar{m}_{\text{NH}_3}^{\text{in}}$, $\bar{m}_{\text{CO}_2}^{\text{in}}$) of the liquid entering the calorimeter and the total mass flow through the calorimeter (i.e., the masses of the liquid and vapor phases, ($\tilde{m}_{\text{liq}}$, $\tilde{m}_{\text{gas}}$) leaving the calorimeter):

$$\bar{n}_{i,\text{liq}}^{\text{in}} = (\tilde{m}_{\text{gas}} + \tilde{m}_{\text{liq}})\frac{\bar{m}_i^{\text{in}}}{\sum_j \bar{m}_j^{\text{in}} M_j} \qquad (i,\ j) = \text{NH}_3,\ \text{CO}_2,\ \text{H}_2\text{O} \quad (22)$$

3. Third, introducing the mole fraction y_i of component i in the vapor leaving the calorimeter into eq 10 results in:

$$\bar{n}_{i,\text{liq}}^{\text{out}} = \bar{n}_{i,\text{liq}}^{\text{in}} - \tilde{m}_{\text{gas}}\frac{y_i}{\sum_j y_j M_j} \qquad (i,\ j) = \text{NH}_3,\ \text{CO}_2,\ \text{H}_2\text{O} \quad (23)$$

Table 5. Experimental Results for the Heat of Evaporation of Pure Water

T^{in}, K	T^{out}, K	$\tilde{m}_{\text{gas}}$, g	$\tilde{m}_{\text{liq}}$, g	ΔH_{exp}, kJ	$\Delta h^{\text{v}}_{\text{exp}}$, J/g	$\Delta h^{\text{v}}_{\text{cal}}$, J/g	$\delta(\Delta h^{\text{v}})$, %	p_{exp}, kPa	p_{cal}, kPa	$\dot{Q}_{\text{el}}$, W
333.4	335.8	6.394	66.78	15.647	2333 ± 16	2351	−0.8	22.5 ± 0.45	22.5	8.7
333.4	335.8	6.408	65.97	15.645	2329 ± 16	2351	−1.0	22.5 ± 0.45	22.5	
333.4	335.8	6.302	86.83	15.645	2335 ± 16	2351	−0.7	22.5 ± 0.45	22.5	
333.4	335.8	6.299	85.11	15.648	2340 ± 16	2351	−0.5	22.5 ± 0.45	22.5	
333.4	335.8	6.247	85.73	15.646	2356 ± 16	2351	0.2	22.5 ± 0.45	22.5	
333.5	335.7	6.272	79.12	15.656	2366 ± 16	2352	0.6	22.5 ± 0.45	22.4	
333.5	335.8	6.284	86.35	15.647	2345 ± 16	2351	−0.3	22.5 ± 0.45	22.5	
333.5	335.8	6.215	90.67	15.645	2363 ± 16	2351	0.5	22.5 ± 0.45	22.5	
333.4	335.9	7.244	33.86	17.602	2370 ± 10	2351	0.8	22.6 ± 0.45	22.6	19.6
333.4	335.8	7.320	33.96	17.600	2347 ± 10	2351	−0.2	22.5 ± 0.45	22.5	
333.5	335.8	7.271	36.25	17.604	2363 ± 10	2352	0.5	22.6 ± 0.45	22.5	
333.5	335.8	3.213	86.77	8.419	2344 ± 33	2351	−0.3	22.5 ± 0.45	22.5	4.7
333.5	335.8	3.215	90.95	8.420	2332 ± 33	2351	−0.8	22.5 ± 0.45	22.5	
333.5	335.8	3.225	85.26	8.418	2345 ± 33	2351	−0.3	22.5 ± 0.45	22.5	
333.5	343.1	6.577	83.08	18.913	2327 ± 17	2334	−0.3	31.1 ± 0.48	31.0	10.5
333.4	342.9	6.554	83.66	18.915	2341 ± 17	2334	0.3	30.9 ± 0.48	30.8	
333.4	342.9	6.523	89.15	18.912	2317 ± 17	2334	−0.7	30.9 ± 0.48	30.9	
333.5	342.8	6.572	86.38	18.912	2326 ± 17	2334	−0.4	30.9 ± 0.48	30.7	
333.5	342.8	6.533	85.56	18.912	2342 ± 17	2334	0.3	30.8 ± 0.48	30.7	
333.5	353.1	6.503	82.54	22.472	2331 ± 18	2309	1.0	47.5 ± 0.54	47.2	12.5
333.5	353.1	6.572	81.75	22.482	2314 ± 18	2308	0.3	47.5 ± 0.54	47.3	
333.5	353.1	6.478	84.05	22.485	2323 ± 18	2309	0.6	47.4 ± 0.54	47.2	
393.3	395.0	4.555	42.59	10.329	2193 ± 15	2197	−0.2	211.5 ± 1	210.2	8.7
393.3	395.0	4.510	43.20	10.326	2213 ± 15	2197	0.7	211.5 ± 1	210.2	
393.1	395.0	4.512	43.43	10.321	2200 ± 15	2197	0.1	211.5 ± 1	210.5	
393.0	395.1	4.500	45.77	10.319	2196 ± 15	2197	0.0	211.5 ± 1	210.8	
393.3	403.0	3.799	44.20	10.238	2172 ± 20	2174	−0.1	268.2 ± 1.4	269.0	8.6
393.3	403.1	3.832	46.06	10.345	2157 ± 20	2174	−0.8	268.2 ± 1.4	269.4	
393.2	402.9	3.781	43.43	10.272	2202 ± 20	2175	1.2	268.6 ± 1.4	268.2	
393.2	412.9	2.781	48.47	10.257	2146 ± 28	2146	0.0	358.2 ± 1.6	358.1	8.5
393.3	412.6	2.958	45.47	10.257	2121 ± 28	2146	−1.2	356.5 ± 1.6	355.3	
393.3	412.6	2.999	44.02	10.250	2128 ± 28	2146	−0.8	356.6 ± 1.6	355.6	
						$\bar{\delta}_{\text{rel}}(\Delta h^{\text{v}}) = 0.5\%$				
					Experimental Uncertainties Not Mentioned					
0.1	0.1	≤0.013	≤0.1	≤0.04%					≤0.03%	

Equation 23 is used together with eqs 3 and 6 and the measured temperature T^{out} to calculate the overall amounts of ammonia, carbon dioxide, and water in the liquid phase as well as the true composition of the liquid leaving the calorimeter in an iterative procedure. Furthermore, the total pressure and the composition of the vapor phase leaving the calorimeter are calculated by applying eqs 7 and 8.

4. Finally, the enthalpy change upon partial evaporation is calculated from eq 18 using the aforementioned results for the true number of moles of the liquid streams entering and leaving the calorimeter as well as the calculated composition of the vapor phase.

Results

Test of Procedure: Enthalpy of Vaporization of Pure Water. To test the experimental arrangement and procedure, the enthalpy of vaporization of pure water was measured. The results for the measured enthalpy changes as well as the measured vapor pressures are given in Table 5. Table 5 also contains numbers for the temperatures at the inlet and outlet of the calorimeter as well as the masses of the liquid ($\tilde{m}_{\text{liq}}$) and gaseous phase ($\tilde{m}_{\text{gas}}$) leaving the calorimeter. Furthermore, results for the enthalpy of evaporation $\Delta h^{\text{v}}_{\text{exp}}$ of pure water calculated from the measured enthalpy change (see following) are given. The temperature of liquid water entering the calorimeter was either 333 or 393 K. The temperatures at the outlet of the calorimeter ranged from 335 to 412 K. The mass flow rate was ~0.05 g/s. At 333 K, the ratio $\tilde{m}_{\text{gas}}/(\tilde{m}_{\text{liq}} + \tilde{m}_{\text{gas}})$ was varied from 6 to 18% by varying the electrical power between 4.7 and 20 W. Within those limits, no influence of the electrical power on the experimental results for the enthalpy of vaporization could be detected, so at 393 K, the electrical power was held constant (≈8.6 W). The enthalpy change in the calorimeter is

$$\Delta H_{\text{exp}} = \tilde{m}_{\text{gas}} h^{\text{s}}_{\text{w,gas}}(T^{\text{out}}) + \tilde{m}_{\text{liq}} h^{\text{s}}_{\text{w,liq}}(T^{\text{out}}) - (\tilde{m}_{\text{gas}} + \tilde{m}_{\text{liq}}) h_{\text{w,liq}}(T^{\text{in}},p) \quad (24)$$

Neglecting the (small) influence of pressure on the enthalpy of liquid water (i.e. $h_{\text{w,liq}}(T^{\text{in}},p) \approx h^{\text{s}}_{\text{w,liq}}(T^{\text{in}})$) that equation may be rearranged to yield the experimental results for the enthalpy of vaporization of pure water at T^{out}

$$\Delta h^{\text{v}}_{\text{w,exp}}(T^{\text{out}}) = h^{\text{s}}_{\text{w,gas}}(T^{\text{out}}) - h^{\text{s}}_{\text{w,liq}}(T^{\text{out}}) = \frac{\Delta H_{\text{exp}} - (\tilde{m}_{\text{gas}} + \tilde{m}_{\text{liq}})(h^{\text{s}}_{\text{w,liq}}(T^{\text{out}}) - h^{\text{s}}_{\text{w,liq}}(T^{\text{in}}))}{\tilde{m}_{\text{gas}}} \quad (25)$$

The second term in the numerator of eq 25 is a correction due to heating the subcooled liquid water to the boiling point temperature. The enthalpies of pure

Table 6. Experimental Results for the Enthalpy Change upon Partial Evaporation of Aqueous Solutions Containing Ammonia

T^{in}, K	T^{out}, K	$\bar{m}_{NH_3}^{in}$, mol/kg	$10 \times p_{exp}$, MPa	$\tilde{m}_{gas}$, g	$\tilde{m}_{liq}$, g	ΔH_{exp}, kJ	$\bar{m}_{NH_3,liq}^{out}$, mol/kg	$\dot{Q}_{el}$, W
313.5	325.2	6.023	0.337 ± 0.007	4.473 ± 0.010	65.82 ± 0.08	12.590 ± 0.127	3.62 ± 0.06	7.0
313.5	325.3	6.023	0.338 ± 0.007	4.417 ± 0.010	66.34 ± 0.08	12.587 ± 0.128	3.69 ± 0.07	7.0
313.5	324.9	11.916	0.661 ± 0.011	3.909 ± 0.011	62.18 ± 0.08	10.807 ± 0.128	8.65 ± 0.14	6.0
313.5	324.8	11.916	0.660 ± 0.011	3.936 ± 0.011	62.45 ± 0.08	10.802 ± 0.128	8.65 ± 0.14	6.0
334.1	339.5	1.580	0.349 ± 0.006	4.343 ± 0.010	86.50 ± 0.08	11.752 ± 0.123	0.96 ± 0.02	6.5
334.1	339.5	1.580	0.349 ± 0.006	4.353 ± 0.010	87.94 ± 0.08	11.751 ± 0.124	0.91 ± 0.02	6.5
334.1	340.9	3.091	0.473 ± 0.007	4.245 ± 0.010	87.41 ± 0.08	11.751 ± 0.130	2.00 ± 0.04	6.5
334.1	341.0	3.091	0.473 ± 0.007	4.241 ± 0.010	86.50 ± 0.08	11.759 ± 0.129	2.02 ± 0.04	6.5
334.1	341.0	3.091	0.473 ± 0.007	4.244 ± 0.010	87.67 ± 0.08	11.749 ± 0.130	2.01 ± 0.04	6.5
333.5	342.5	6.217	0.749 ± 0.012	2.495 ± 0.012	42.89 ± 0.08	6.954 ± 0.100	4.11 ± 0.08	3.9
333.5	342.5	6.217	0.749 ± 0.012	2.542 ± 0.012	44.31 ± 0.08	6.943 ± 0.101	4.22 ± 0.08	3.8
333.4	343.7	6.217	0.750 ± 0.010	4.248 ± 0.012	62.28 ± 0.08	11.747 ± 0.123	3.97 ± 0.07	6.5
333.4	343.7	6.217	0.750 ± 0.010	4.297 ± 0.012	65.58 ± 0.08	11.745 ± 0.126	3.97 ± 0.07	6.5
333.1	342.1	8.960	1.023 ± 0.012	4.269 ± 0.013	85.92 ± 0.09	11.769 ± 0.144	6.73 ± 0.11	6.5
333.2	342.1	8.960	1.023 ± 0.012	4.294 ± 0.013	84.63 ± 0.09	11.750 ± 0.142	6.74 ± 0.11	6.5
333.2	342.1	8.960	1.023 ± 0.012	4.319 ± 0.013	85.33 ± 0.09	11.749 ± 0.143	6.76 ± 0.11	6.5
333.9	342.3	12.919	1.463 ± 0.016	4.600 ± 0.015	82.82 ± 0.09	11.748 ± 0.144	9.94 ± 0.15	6.5
333.9	342.2	12.919	1.463 ± 0.016	4.564 ± 0.015	83.44 ± 0.09	11.746 ± 0.144	10.08 ± 0.15	6.5
352.8	358.4	1.580	0.744 ± 0.008	4.394 ± 0.012	88.05 ± 0.08	11.715 ± 0.129	1.00 ± 0.02	6.5
352.8	358.5	1.580	0.744 ± 0.008	4.379 ± 0.012	88.53 ± 0.08	11.714 ± 0.130	1.00 ± 0.02	6.5
353.1	360.4	3.036	0.968 ± 0.010	4.532 ± 0.013	69.84 ± 0.09	11.706 ± 0.122		6.5
353.9	360.3	3.195	0.977 ± 0.010	4.520 ± 0.013	78.08 ± 0.09	11.711 ± 0.126	2.04 ± 0.04	6.5
354.0	360.3	3.195	0.977 ± 0.010	4.603 ± 0.013	78.33 ± 0.09	11.708 ± 0.126	2.04 ± 0.04	6.5
354.4	362.7	5.831	1.450 ± 0.015	4.506 ± 0.015	70.99 ± 0.09	11.728 ± 0.132	3.95 ± 0.07	6.5
354.8	362.0	5.831	1.451 ± 0.014	4.549 ± 0.015	75.07 ± 0.09	11.703 ± 0.132	4.05 ± 0.07	6.5
353.3	362.1	8.802	1.960 ± 0.019	4.529 ± 0.018	72.68 ± 0.09	11.704 ± 0.141	6.46 ± 0.11	6.5
353.4	362.3	8.802	1.960 ± 0.020	4.541 ± 0.018	70.47 ± 0.09	11.710 ± 0.140	6.42 ± 0.11	6.5
354.0	362.6	12.109	2.677 ± 0.028	4.754 ± 0.021	71.82 ± 0.10	11.703 ± 0.148	9.32 ± 0.15	6.5
353.5	362.3	12.109	2.672 ± 0.027	4.668 ± 0.021	73.81 ± 0.10	11.706 ± 0.151	9.44 ± 0.15	6.5
353.4	362.7	12.109	2.677 ± 0.028	4.701 ± 0.021	71.52 ± 0.10	11.703 ± 0.150	9.40 ± 0.15	6.5
393.4	401.5	6.017	4.659 ± 0.038	5.301 ± 0.031	65.02 ± 0.11	12.479 ± 0.165	3.94 ± 0.08	6.9
393.4	401.6	6.017	4.660 ± 0.038	5.260 ± 0.031	66.47 ± 0.11	12.476 ± 0.167	4.01 ± 0.08	6.9
393.2	402.4	12.010	7.680 ± 0.105	4.977 ± 0.046	62.99 ± 0.13	11.575 ± 0.199		6.4
393.2	402.4	12.010	7.670 ± 0.103	4.931 ± 0.046	67.08 ± 0.13	11.583 ± 0.203	8.73 ± 0.16	6.4
393.2	402.3	12.010	7.670 ± 0.105	5.056 ± 0.046	62.99 ± 0.13	11.574 ± 0.198	8.81 ± 0.17	6.4
					Experimental Uncertainties Not Mentioned			
0.1	0.1	≤0.3%						≤0.03%

liquid water $h_{w,liq}^{s}(T)$ are taken from Saul and Wagner (1987). The experimental results for the enthalpy of vaporization as calculated from eq 25 are compared with results calculated from the correlation by Saul and Wagner (1987) (see $\Delta h_{w,cal}^{v}$ in Table 5). As can be seen from that comparison, in most cases, the relative deviation does not exceed 0.5%, thus confirming our experimental equipment and procedure. The relative deviations of the experimental results for the vapor pressure from a vapor pressure equation by Saul and Wagner (1987; see p_{cal} in Table 5) do not exceed 0.7% and are always within the experimental uncertainties of the pressure measurement of the present work.

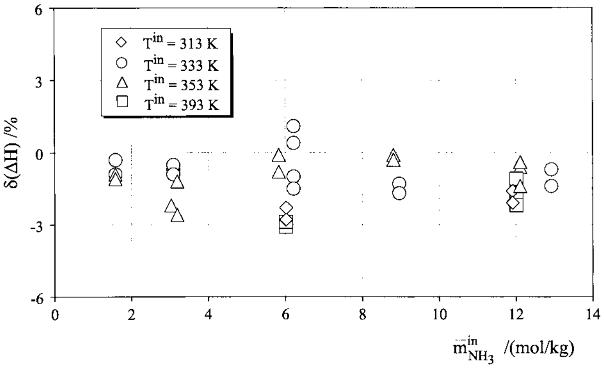

Figure 4. NH_3-H_2O: Relative deviations between predicted and measured enthalpy changes upon partial evaporation.

Enthalpy of Vaporization of Aqueous Solutions of Ammonia. The experimental results for the enthalpy change upon partial evaporation of aqueous ammonia solutions are given in Table 6. The temperature of the liquid solution entering the calorimeter ranged from 313 to 393 K. Outlet temperatures were from ~325 to 402 K. The overall molality of ammonia entering the calorimeter ranged from ~1.6 to 12 mol/kg. The electrical power supplied to the calorimeter ranged from 6.4 to 7 W. Thus, ~5−8% of the subcooled liquid entering the calorimeter was evaporated. The typical running time for an experiment was ~30 min. In the concentration range considered here, the protolysis of ammonia has no influence. The enthalpy change upon partial evaporation of aqueous ammonia solutions thus results from heating the subcooled liquid stream and from the enthalpy effect due to the partial evaporation of the liquid mixture (i.e., the two contributions in eq 18 resulting from chemical reactions are negligible). Figure 4 shows the relative deviations

$$\delta(\Delta H) = (\Delta H_{exp} - \Delta H_{cal})/\Delta H_{cal} \qquad (26)$$

of the experimental results for the enthalpy change (ΔH_{exp}) from numbers predicted by the model (ΔH_{cal}). The average and maximum relative deviations are 1.3 and 3%, respectively.

In Figures 5 and 6, similar comparisons are shown for the total pressure and the overall molality of

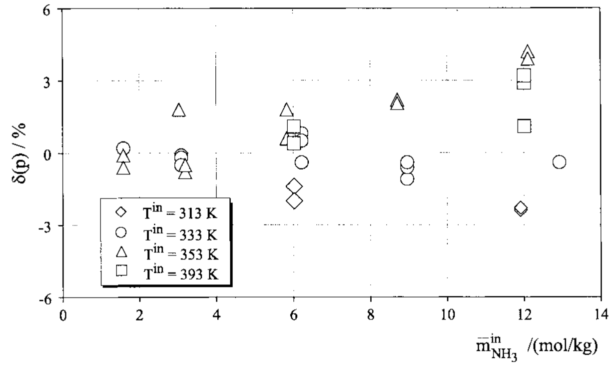

Figure 5. NH_3-H_2O: Relative deviations between predicted and measured total pressures upon partial evaporation.

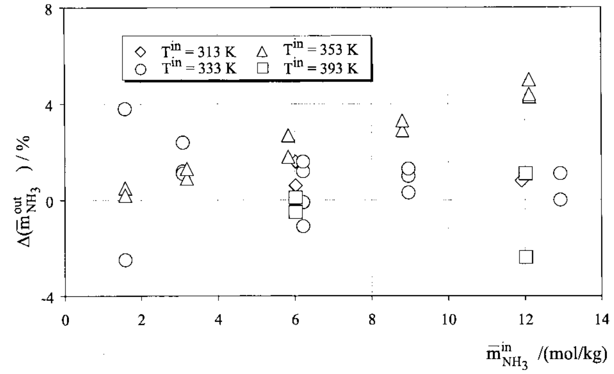

Figure 6. NH_3-H_2O: Relative deviations between predicted and measured overall molalities of ammonia in the liquid phase leaving the calorimeter.

Table 7. Calculated Contributions to the Enthalpy Change upon Partial Evaporation of an Aqueous Ammoniacal Solution

Experimental Data

T^{in}, K	T^{out}, K	$\bar{m}^{in}_{NH_3}$, mol/kg	$\bar{m}^{out}_{NH_3}$, mol/kg	$\tilde{m}_{gas}$, g	$\tilde{m}_{liq}$, g	ΔH_{exp}, kJ
333.9	342.3	12.919	9.94	4.60	82.82	11.748

Calculated Results

parameter	kJ	relative contribution, %
$\sum n^{in}_{i,liq}(h^{Ref}_{i,liq}(T^{out}) - h^{Ref}_{i,liq}(T^{in}))$	3.217	27.0
$\sum_i n^{in}_{i,liq}(h^{E}_{i,liq}(T^{out},m^{out}_j) - h^{E}_{i,liq}(T^{in},m^{in}_j))$	−0.074	−0.6
$\sum_i n^{out}_{i,gas}(h_{i,gas}(T^{out},p,y_j) - h_{i,liq}(T^{out},p,m^{out}_j))$	8.777	73.6
$\sum$	11.922	100

ammonia in the liquid phase leaving the calorimeter. Indices “exp” and “cal” indicate the direct experimental results and the results calculated while evaluating some of the experimental data as described before (see section *Evaluation of the Experimental Results*). The average relative deviations are 1.3% in the total pressure and 1.7% in the molality of ammonia. The maximum relative deviations are 3 and 4%, respectively.

Table 7 shows calculated absolute and relative contributions to the enthalpy change (according to eq 18) for a typical experiment at 334 K. In that experiment, the liquid mixture entering the calorimeter was heated from ~334 to 342 K. About 5% of the liquid was evaporated. About 27% of the enthalpy change results from heating the subcooled liquid mixture from T^{in} to T^{out}, whereas ~74% is due to the partial evaporation of ammonia and water. As was expected, in the system NH_3-H_2O, the effects due to the nonideality of the liquid solution contribute only a small amount to the total enthalpy change [in total ~1.2%; 0.6% from the second term on the right-hand side of eq 18 (see also Table 7) and another 0.6% from the liquid phase enthalpies in the fourth term].

Enthalpy of Evaporation of Aqueous Solutions Containing Ammonia and Carbon Dioxide. The experimental results for the enthalpy change upon partial evaporation of aqueous solutions containing ammonia and carbon dioxide are given in Table 8. The overall molality of ammonia in the liquid stream entering the calorimeter $\bar{m}^{in}_{NH_3}$ was ~6 and 12 mol/kg. The ratio $\bar{m}^{in}_{NH_3}/\bar{m}^{in}_{CO_2}$ was varied between 2 and 4. The temperature of the liquid stream entering the calorimeter ranged from 313 to 393 K. The electrical power ranged from ~3 to 9 W; thus, ~3.5−11% of the liquid stream was evaporated. The total pressure ranged up to 2 MPa.

Figure 7 shows relative deviations between measured and predicted results for the enthalpy change. Figures 8 to 10 show relative deviations between the experimental results for the total pressure and the overall molalities of ammonia and carbon dioxide in the liquid phase leaving the calorimeter and those determined in the evaluation of some of the experimental results as already described (see section *Evaluation of the Experimental Results*) for the series of measurements at 333 K and $\bar{m}^{in}_{NH_3}$ = 6 and 12 mol/kg.

For those two series of measurements, predicted enthalpy changes deviate by <5% from the experimental results. The deviations slightly increase with increasing overall amount of carbon dioxide dissolved in the liquid phase. The scattering of the data shown in Figure 7 also reveals some experimental difficulties especially at higher pressures. For example, at $\bar{m}^{in}_{NH_3}$ = 12 mol/kg and $\bar{m}^{in}_{CO_2}$ = 6 mol/kg, deviations scatter by ~2% around the arithmetic average. At these conditions, small changes in the holdup of the calorimeter as well as small amounts of liquid droplets entrained in the gaseous phase cause large deviations in the calculated enthalpy change.

Calculated total pressures deviate by about −6 to 4% from the direct experimental results. Similar deviations are found for the calculated overall molality of ammonia at the outlet. However, as is shown in Figure 10 larger relative deviations are observed in the overall molality of carbon dioxide ranging up to 8%. Again, the scattering of the data especially at ratios $\bar{m}^{in}_{CO_2}/\bar{m}^{in}_{NH_3} \approx 1$ (where the total pressure steeply rises with increasing amount of carbon dioxide) shows the experimental difficulties in determining the enthalpy change upon partial evaporation under those extreme conditions.

Table 9 shows the calculated absolute and relative contributions to the enthalpy change for a typical experiment at 333 K. In that experiment, the liquid mixture entered the calorimeter at 333.4 K. The outlet temperature was 341.3 K. About 8.6% of the liquid mixture was vaporized, resulting in an experimental enthalpy change of ~15.6 kJ. The calculated enthalpy change is 15.28 kJ. About 1.96 kJ or 12.8% of the total enthalpy change result from heating the liquid mixture to the boiling point temperature (first term in eq 18). The change in the extent of the chemical reactions (third term in eq 18) contributes ~5.3 kJ or 34.9% to the enthalpy change. The enthalpy change due to the

Table 8. Experimental Results for the Enthalpy Change upon Partial Evaporation of Aqueous Solutions Containing Ammonia and Carbon Dioxide

T^{in}, K	T^{out}, K	$\bar{m}^{\mathrm{in}}_{\mathrm{NH_3}}$, mol/kg	$\bar{m}^{\mathrm{in}}_{\mathrm{CO_2}}$, mol/kg	$10 \times p_{\mathrm{exp}}$, MPa	$\tilde{m}_{\mathrm{gas}}$, g	$\tilde{m}_{\mathrm{liq}}$, g	ΔH_{exp}, kJ	$\bar{m}^{\mathrm{out}}_{\mathrm{NH_3,liq}}$, mol/kg	$\bar{m}^{\mathrm{out}}_{\mathrm{CO_2,liq}}$, mol/kg	$\dot{Q}_{\mathrm{el}}$, W
313.5	324.8	5.975	1.527	0.256 ± 0.006	4.271 ± 0.009	70.32 ± 0.08	12.587 ± 0.125	4.40 ± 0.09	1.37 ± 0.03	7.0
313.5	324.8	5.975	1.527	0.256 ± 0.006	4.290 ± 0.009	70.82 ± 0.08	12.596 ± 0.125	4.36 ± 0.09	1.41 ± 0.03	7.0
313.5	319.9	6.022	3.011	0.174 ± 0.005	5.375 ± 0.009	43.47 ± 0.08	12.624 ± 0.079	4.47 ± 0.10	2.31 ± 0.05	7.0
313.5	320.0	6.022	3.011	0.174 ± 0.005	5.355 ± 0.009	43.26 ± 0.08	12.626 ± 0.079	4.39 ± 0.10	2.26 ± 0.05	7.0
313.5	326.8	11.767	3.000	0.473 ± 0.008	3.483 ± 0.010	73.14 ± 0.08	10.799 ± 0.131	9.63 ± 0.21	2.96 ± 0.07	6.0
313.5	326.8	11.767	3.000	0.474 ± 0.008	3.454 ± 0.010	73.03 ± 0.08	10.800 ± 0.131	9.59 ± 0.21	2.96 ± 0.07	6.0
313.5	321.6	11.841	5.921	0.258 ± 0.006	4.754 ± 0.009	31.72 ± 0.08	10.815 ± 0.076	9.23 ± 0.24	4.43 ± 0.12	6.0
313.5	321.6	11.841	5.921	0.256 ± 0.006	4.672 ± 0.009	39.62 ± 0.08	10.812 ± 0.083	9.22 ± 0.23	4.71 ± 0.12	6.0
313.2	320.9	12.060	6.030	0.250 ± 0.006	6.661 ± 0.009	80.58 ± 0.08	15.671 ± 0.118	9.69 ± 0.22	5.28 ± 0.12	8.7
313.2	320.9	12.060	6.030	0.249 ± 0.006	6.639 ± 0.009	78.94 ± 0.08	15.635 ± 0.116	9.44 ± 0.22	5.13 ± 0.12	8.7
333.7	341.7	6.356	1.571	0.572 ± 0.007	6.335 ± 0.011	66.37 ± 0.08	15.629 ± 0.114			8.7
333.6	342.0	6.356	1.571	0.574 ± 0.007	6.302 ± 0.011	67.54 ± 0.08	15.635 ± 0.117	4.30 ± 0.09	1.21 ± 0.03	8.7
333.6	342.0	6.356	1.571	0.573 ± 0.007	6.367 ± 0.011	67.68 ± 0.08	15.631 ± 0.117			8.7
333.9	341.6	5.820	1.515	0.550 ± 0.007	6.245 ± 0.011	79.95 ± 0.08	15.628 ± 0.125	4.10 ± 0.08	1.23 ± 0.03	8.7
333.9	341.7	5.820	1.515	0.550 ± 0.007	6.210 ± 0.011	80.05 ± 0.08	15.622 ± 0.125	4.13 ± 0.08	1.14 ± 0.02	8.7
333.7	342.8	6.017	3.115	0.664 ± 0.008	6.405 ± 0.011	76.02 ± 0.08	15.622 ± 0.121	5.15 ± 0.11	2.28 ± 0.05	8.7
333.7	342.9	6.017	3.115	0.660 ± 0.008	6.434 ± 0.011	82.18 ± 0.08	15.624 ± 0.126	5.11 ± 0.10	2.26 ± 0.05	8.7
333.7	340.2	5.578	2.789	0.550 ± 0.007	6.584 ± 0.011	96.39 ± 0.08	15.634 ± 0.129	4.76 ± 0.09	2.13 ± 0.04	8.7
333.7	340.3	5.578	2.789	0.551 ± 0.007	6.628 ± 0.011	92.33 ± 0.08	15.634 ± 0.126	4.68 ± 0.09	2.08 ± 0.04	8.7
333.7	340.2	6.747	3.374	0.574 ± 0.008	7.091 ± 0.011	71.11 ± 0.08	15.637 ± 0.107	5.30 ± 0.11	2.28 ± 0.05	8.7
333.7	340.2	6.747	3.374	0.576 ± 0.008	7.033 ± 0.011	70.92 ± 0.08	15.636 ± 0.107	5.37 ± 0.11	2.30 ± 0.05	8.7
333.9	340.3	6.155	3.078	0.570 ± 0.007	6.844 ± 0.011	82.10 ± 0.08	15.628 ± 0.116	5.02 ± 0.10	2.26 ± 0.05	8.7
333.9	340.6	6.155	3.078	0.570 ± 0.007	6.849 ± 0.011	80.92 ± 0.08	15.624 ± 0.117	4.94 ± 0.10	2.23 ± 0.05	8.7
333.7	339.5	5.972	2.986	0.549 ± 0.008	3.375 ± 0.011	42.19 ± 0.08	7.611 ± 0.078	4.77 ± 0.10	2.14 ± 0.05	4.2
333.7	339.5	5.972	2.986	0.549 ± 0.008	3.333 ± 0.011	40.20 ± 0.08	7.612 ± 0.076	4.90 ± 0.11	2.14 ± 0.05	4.2
333.6	338.7	5.972	2.986	0.549 ± 0.008	3.257 ± 0.011	56.84 ± 0.08	7.621 ± 0.088	5.20 ± 0.11	2.37 ± 0.05	4.2
333.6	338.6	5.972	2.986	0.549 ± 0.008	3.251 ± 0.011	62.52 ± 0.08	7.626 ± 0.093	5.24 ± 0.11	2.31 ± 0.05	4.2
333.6	338.8	5.898	2.949	0.549 ± 0.008	3.191 ± 0.011	66.11 ± 0.08	7.485 ± 0.097	5.25 ± 0.11	2.40 ± 0.05	2.8
333.6	338.8	5.898	2.949	0.549 ± 0.008	3.159 ± 0.011	69.32 ± 0.08	7.484 ± 0.100	5.26 ± 0.11	2.37 ± 0.05	2.8
334.0	345.2	12.015	2.959	1.000 ± 0.011	5.987 ± 0.013	79.34 ± 0.09	15.613 ± 0.137			8.7
333.9	345.1	12.015	2.959	1.000 ± 0.011	5.962 ± 0.013	80.61 ± 0.09	15.604 ± 0.138			8.7
333.5	343.0	11.637	2.898	0.997 ± 0.010	5.649 ± 0.013	116.35 ± 0.09	15.609 ± 0.161			8.7
333.5	344.3	11.637	2.898	0.997 ± 0.010	6.029 ± 0.013	89.93 ± 0.09	15.610 ± 0.144	9.40 ± 0.20	2.68 ± 0.06	8.7
333.5	344.2	11.637	2.898	0.997 ± 0.010	5.868 ± 0.013	89.93 ± 0.09	15.607 ± 0.144	9.46 ± 0.20	2.71 ± 0.06	8.7
333.5	344.3	11.637	2.898	0.997 ± 0.010	5.802 ± 0.013	90.73 ± 0.09	15.622 ± 0.145	9.39 ± 0.20	2.70 ± 0.06	8.7
333.5	344.2	11.637	2.898	0.997 ± 0.010	5.926 ± 0.013	93.12 ± 0.09	15.617 ± 0.146	9.33 ± 0.20	2.67 ± 0.06	8.7
334.5	340.9	11.582	5.791	0.792 ± 0.009	7.091 ± 0.012	88.10 ± 0.08	15.620 ± 0.121			8.7
333.5	340.9	11.582	5.791	0.793 ± 0.009	6.911 ± 0.012	86.88 ± 0.08	15.616 ± 0.124			8.7
333.4	343.4	11.463	5.732	0.793 ± 0.011	7.103 ± 0.012	33.85 ± 0.08	15.610 ± 0.085	7.84 ± 0.20	3.52 ± 0.09	8.7
333.4	343.1	11.463	5.732	0.793 ± 0.011	7.070 ± 0.012	35.13 ± 0.08	15.608 ± 0.085	7.86 ± 0.20	3.65 ± 0.09	8.7
333.4	341.3	11.463	5.732	0.793 ± 0.009	6.931 ± 0.012	73.59 ± 0.08	15.612 ± 0.115	9.71 ± 0.22	4.53 ± 0.11	8.7
333.4	341.2	11.463	5.732	0.793 ± 0.009	7.011 ± 0.012	75.55 ± 0.08	15.609 ± 0.116	9.73 ± 0.22	4.53 ± 0.11	8.7
333.5	340.8	11.930	5.965	0.793 ± 0.011	3.389 ± 0.012	33.47 ± 0.08	7.627 ± 0.076	10.17 ± 0.26	4.62 ± 0.12	4.2
333.5	340.9	11.930	5.965	0.793 ± 0.011	3.382 ± 0.012	36.51 ± 0.08	7.630 ± 0.079	10.11 ± 0.26	4.66 ±0.12	4.2
333.5	340.2	11.930	5.965	0.793 ± 0.010	3.302 ± 0.012	51.94 ± 0.08	7.628 ± 0.090	10.62 ± 0.26	4.96 ± 0.12	4.2
333.5	340.0	11.930	5.965	0.793 ± 0.010	3.288 ± 0.012	56.54 ± 0.08	7.628 ± 0.093	10.68 ± 0.26	4.86 ± 0.12	4.2
333.5	339.7	11.706	5.853	0.795 ± 0.010	3.042 ± 0.012	71.95 ± 0.08	7.493 ± 0.105	10.93 ± 0.26	5.23 ± 0.13	2.8
333.5	339.7	11.706	5.853	0.794 ± 0.010	2.975 ± 0.012	71.95 ± 0.08	7.492 ± 0.106	10.99 ± 0.26	5.26 ± 0.13	2.8
353.6	359.3	5.820	1.515	1.149 ± 0.011	6.811 ± 0.014	67.19 ± 0.09	15.570 ± 0.113	0.00 ± 0.08	0.00 ± 0.13	8.7
353.7	359.3	5.820	1.515	1.149 ± 0.011	6.735 ± 0.014	67.69 ± 0.09	15.571 ± 0.113	3.94 ± 0.08	0.98 ± 0.02	8.7
353.6	361.9	6.155	3.078	1.621 ± 0.015	6.736 ± 0.016	83.71 ± 0.09	15.575 ± 0.134	5.17 ± 0.11	1.99 ± 0.04	8.7
353.6	362.0	6.155	3.078	1.621 ± 0.015	6.753 ± 0.016	84.03 ± 0.09	15.575 ± 0.134	5.14 ± 0.10	2.01 ± 0.04	8.7
353.2	361.0	6.020	3.010	1.602 ± 0.015	5.002 ± 0.016	74.14 ± 0.09	11.778 ± 0.123			6.5
353.2	361.0	6.020	3.010	1.602 ± 0.015	4.963 ± 0.016	74.75 ± 0.09	11.712 ± 0.123			6.5
353.4	362.2	6.757	3.379	1.672 ± 0.015	6.919 ± 0.016	71.13 ± 0.09	15.576 ± 0.125	5.50 ± 0.11	1.95 ± 0.04	8.7
353.7	361.3	12.015	2.959	1.899 ± 0.016	6.662 ± 0.017	79.55 ± 0.09	15.566 ± 0.134			8.6
353.2	361.2	11.637	2.898	1.909 ± 0.015	6.505 ± 0.018	80.39 ± 0.09	15.572 ± 0.137	9.23 ± 0.20	2.42 ± 0.06	8.7
353.2	361.2	11.637	2.898	1.910 ± 0.015	6.482 ± 0.018	81.02 ± 0.09	15.571 ± 0.137	9.25 ± 0.20	2.46 ± 0.06	8.7
353.2	361.1	11.463	5.732	2.291 ± 0.022	4.311 ± 0.019	83.78 ± 0.09	10.377 ± 0.132	10.57 ± 0.25	4.83 ± 0.12	8.7
353.2	363.3	11.497	5.749	2.296 ± 0.021	6.862 ± 0.019	68.20 ± 0.09	15.559 ± 0.130	9.93 ± 0.23	4.18 ± 0.10	8.6
353.2	363.3	11.497	5.749	2.296 ± 0.021	6.878 ± 0.019	68.06 ± 0.09	15.563 ± 0.130	9.90 ± 0.23	4.16 ± 0.10	8.6
393.5	400.0	6.059	1.533	5.302 ± 0.040	5.419 ± 0.035	72.74 ± 0.11	12.487 ± 0.166			6.9
393.4	400.1	6.059	1.533	5.334 ± 0.040	5.464 ± 0.035	73.65 ± 0.11	12.500 ± 0.169	4.83 ± 0.10	0.85 ± 0.02	6.9
393.4	409.1	6.022	3.011	13.970 ± 0.420	3.361 ± 0.078	74.68 ± 0.16	10.697 ± 0.307	5.68 ± 0.13	2.12 ± 0.07	5.9
393.4	409.7	6.065	3.033	14.350 ± 0.480	3.143 ± 0.080	79.04 ± 0.17	10.697 ± 0.319	5.74 ± 0.13	2.11 ± 0.07	5.9
393.2	409.7	5.948	2.974	13.940 ± 0.428	3.401 ± 0.078	77.54 ± 0.16	10.715 ± 0.315	5.22 ± 0.12	1.94 ± 0.06	6.0
393.5	398.3	12.000	3.051	7.110 ± 0.086	6.520 ± 0.044	68.85 ± 0.12	13.468 ± 0.169	9.33 ± 0.22	1.94 ± 0.05	7.5
393.5	398.3	12.000	3.051	7.110 ± 0.085	6.517 ± 0.044	70.93 ± 0.12	13.441 ± 0.170	9.55 ± 0.22	2.11 ± 0.06	7.5
393.1	406.2	11.976	5.988	19.340 ± 0.526	3.495 ± 0.047	84.44 ± 0.20	10.462 ± 0.240			5.8
					Experimental Uncertainties Not Mentioned					
0.1	0.1	≤0.2%	≤0.15%							≤0.04%

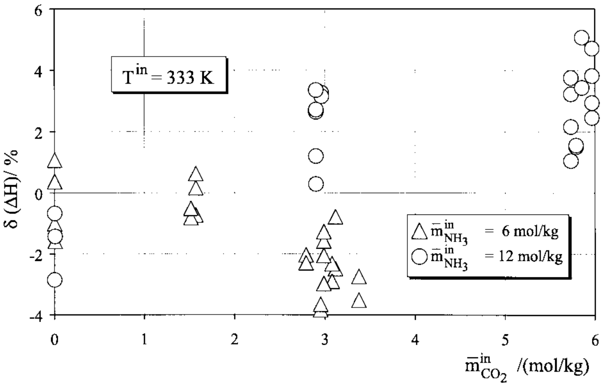

Figure 7. $NH_3-CO_2-H_2O$: Relative deviations between predicted and measured total pressures upon partial evaporation.

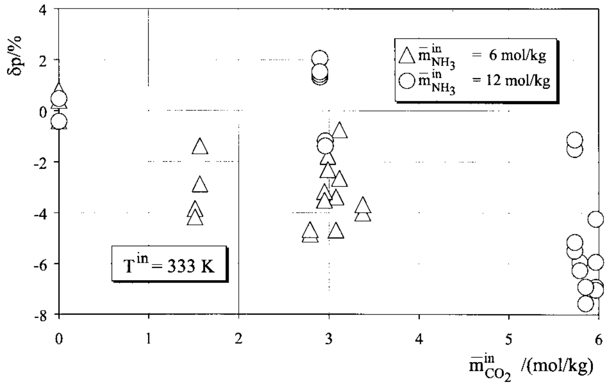

Figure 8. $NH_3-CO_2-H_2O$: Relative deviations between predicted and measured total pressures upon partial evaporation.

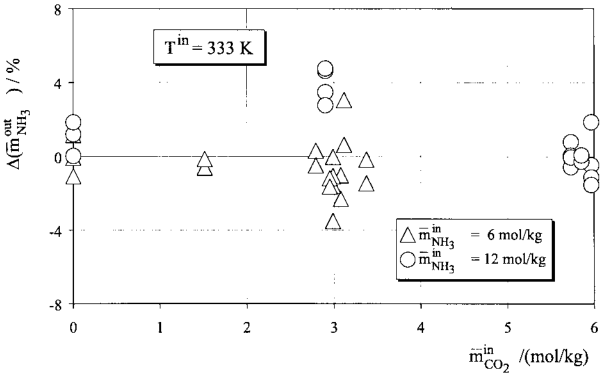

Figure 9. $NH_3-CO_2-H_2O$: Relative deviations between predicted and measured overall molalities of ammonia in the liquid phase leaving the calorimeter.

partial evaporation of the volatile components (fourth term in eq 18) is 7.78 kJ or 50.9% of the total enthalpy change. The effects from the nonideality of the solutions contribute only to a small amount to the total enthalpy change (0.22 kJ or 1.4%). However, it should be clearly noted that the nonideality of the solutions cannot be neglected at all because it has a large influence on the species distribution in the liquid phase and therefore also contributes (through the reactions) to the enthalpy change. That contribution adds ~35% to the total enthalpy change.

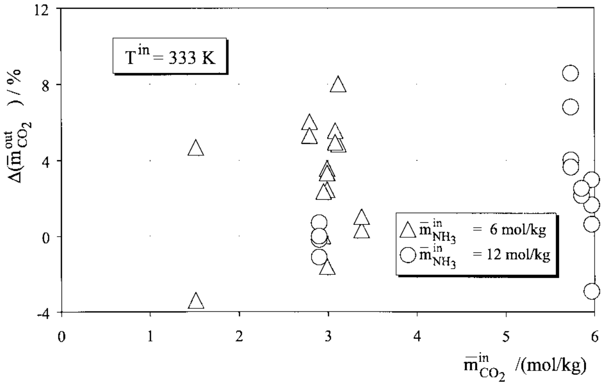

Figure 10. $NH_3-CO_2-H_2O$: Relative deviations between predicted and measured overall molalities of carbon dioxide in the liquid phase leaving the calorimeter.

Table 9. Calculated Contributions to the Enthalpy Change upon Partial Evaporation of an Aqueous Solution Containing Ammonia and Carbon Dioxide

Experimental Data

T^{in}, K	T^{out}, K	$\bar{m}^{in}_{NH_3}$, mol/kg	$\bar{m}^{out}_{NH_3}$, mol/kg	$\bar{m}^{in}_{CO_2}$, mol/kg	$\bar{m}^{out}_{CO_2}$, mol/kg	$\tilde{m}_{gas}$, g	$\tilde{m}_{liq}$, g	ΔH_{exp}, kJ
333.4	341.3	11.463	9.71	5.732	4.53	6.931	73.59	15.612

Calculated Results

parameter	kJ	relative contribution, %
$\sum n^{in}_{i,liq}(h^{Ref}_{i,liq}(T^{out}) - h^{Ref}_{i,liq}(T^{in}))$	1.955	12.8
$\sum_i n^{in}_{i,liq}(h^{E}_{i,liq}(T^{out},p,m_j^{out}) - h^{E}_{i,liq}(T^{in},p,m_j^{in}))$	0.21	1.38
$\sum_R \Delta\xi_R \Delta_R h^{Ref}_{liq}(T^{out})$	5.33	34.88
$\sum_i n^{out}_{i,gas}(h_{i,gas}(T^{out},p,y_j^{out}) - h_{i,liq}(T^{out},m_j^{out}))$	7.78	50.9
$\sum_R \Delta\xi_R \Delta_R h^{E}_{liq}(T^{out},p,m_j^{out})$	0.0056	0.04
$\sum$	15.281	100

In Table 10 (available as *Supporting Information*), measured numbers for the total pressure, the overall molalities of ammonia and carbon dioxide at the outlet, as well as measured enthalpy changes are compared with model predictions (for the enthalpy change) and results from the evaluation already described (see section *Evaluation of the Experimental Results*). As can be seen from that comparison, the relative deviations between measured and predicted enthalpy changes do not exceed 6%. The average relative deviation between predicted and measured enthalpy changes is only ~1.3%.

Conclusions

A thin-film evaporator flow calorimeter was used to determine enthalpy changes upon partial evaporation of aqueous solutions containing ammonia and carbon dioxide. As a test of the experimental equipment and procedure, the enthalpy of vaporization of pure water was determined. The typical relative deviation of the new data from reliable data for the enthalpy of vaporization of water published in the literature is ~0.5%, thus confirming the experimental procedure. However, it has to be mentioned that that procedure is not recommended for investigation of pure substances. Enthalpies of evaporation of aqueous solutions containing ammonia were then measured at temperatures from 313 to 393 K. Next, enthalpy changes upon partial evaporation of aqueous solutions containing ammonia and carbon dioxide were determined over a wide range of temperature and composition. The physicochemical model previously used to describe phase equilibria in aqueous solutions containing ammonia and sour gases is used to derive a predictive enthalpy model. A comparison between the new experimental data for the enthalpy change upon partial evaporation of aqueous solutions containing ammonia and predicted values reveals typical deviations of ~1%. For the system $NH_3-CO_2-H_2O$, the deviations are larger (~1−2%). It is assumed that those larger deviations are mainly due to uncertainties in calculating the liquid phase species distribution. The comparisons reveal that the model is able to quantitatively predict the enthalpy change upon partial evaporation of that complex, chemical reactive mixture.

Acknowledgment

Financial support of this investigation by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Supporting Information Available: Table 10 containing a detailed comparison between the experimental results and model predictions for the system $NH_3-CO_2-H_2O$ (3 pages). Ordering information is given on any current masthead page.

Nomenclature

$A_i...D_i$ = coefficients for the temperature dependence of heat capacities
$A_{i,\mathrm{w}}...E_{i,\mathrm{w}}$ = coefficients for the temperature dependence of Henry's constants
$A_\mathrm{R}...D_\mathrm{R}$ = coefficients for the temperature dependence of equilibrium constants
A_ϕ = Debye−Hückel parameter
$a_{i,i}...d_{i,i}$ = coefficients for the temperature dependence of second virial coefficients
a_i = activity of component i
b = constant in modified Debye−Hückel expression
B_mix = second virial coefficient of gaseous mixture
$B_{i,j}$ = second virial coefficient for interactions between species i and j
c_p = molar heat capacity at constant pressure
D = relative dielectric constant of water
E_kin = kinetic energy
E_pot = potential energy
e = charge of proton
f = function for the temperature dependence of an interaction parameter
f_1, f_2, f_3 = functions in Pitzer's equation
G^E = excess Gibbs energy
h_i = partial molar enthalpy of component i
h_i^E = partial molar excess enthalpy of component i
H = enthalpy
$H_{i,\mathrm{w}}^{(\mathrm{m})}$ = Henry's constant for the solubility of gas i in pure water (on molality scale)
I = ionic strength (on molality scale)
k = Boltzmann constant
K_R = equilibrium constant for chemical reaction R (on molality scale)
M_i = molar mass of component i
$\tilde{m}$ = mass
$\bar{m}_i$ = overall molality of component i
m_i = true molality of component i
$\bar{n}_i$ = overall number of moles of component i
n_i = true number of moles of component i
N_A = Avogadro's number
p = total pressure
q_i = coefficients for the temperature dependence of interaction parameters
Q = heat
R = universal gas constant
T = absolute temperature
$U_1...U_9$ = constants for the temperature dependence of dielectric constant of pure water
v = partial molar volume
W = work
x = variable in Pitzer's equation
y = mole fraction in vapor
z_i = number of charges of component i

Greek Letters

α = constant in Pitzer's equation
$\beta^{(0)}$, $\beta^{(1)}$ = binary interaction parameters in Pitzer's equation
δh = residual part of the partial molar enthalpy
δ, Δ = difference
ϵ_0 = vacuum permittivity
γ^* = activity coefficient normalized to infinite dilution (on molality scale)
$\nu_{i,\mathrm{R}}$ = stoichiometric coefficient of component i in reaction R ($\nu_{i,\mathrm{R}} > 0$ for products and $\nu_{i,\mathrm{R}} < 0$ for educts)
ρ = mass density
τ = ternary interaction parameter in Pitzer's equation
φ = fugacity coefficient
ξ_R = extent of reaction R

Subscripts

cal = calculated
el = electric
exp = experimental
gas = gas phase
id.gas = in the state of the ideal gas
i, j, k = component i, j, k
liq = liquid phase
mix = mixture
pure = pure component
R = reaction R
w = water

Superscripts

E = excess
in = entering the calorimeter
m = on molality scale
out = leaving the calorimeter
ref = reference state
s = saturation
$*$ = normalized to infinite dilution
∞ = infinite dilution
$\ominus$ = standard state

Appendix: Details on the Calculation of Partial Molar Enthalpies

1. Enthalpies of Gaseous Species. The partial molar enthalpy of a gaseous species i is calculated from the equation

$$h_{i,\mathrm{gas}}(T,p,y_j) = h_{i,\mathrm{id.gas}}(T) - RT^2\left(\frac{\partial \ln \varphi_{i,\mathrm{gas}}}{\partial T}\right)_{p,y_j} \qquad (27)$$

The enthalpy of a gaseous species i in its reference state is calculated by applying

$$h_{i,\mathrm{id.gas}}(T) = h^{\ominus}_{i,\mathrm{id.gas}}(T^{\ominus}) + \int_{T^{\ominus}}^{T} c_{\mathrm{p},i,\mathrm{id.gas}}\, \mathrm{d}T \qquad (28)$$

where $h^{\ominus}_{i,\mathrm{id.gas}}(T^{\ominus})$ is the standard enthalpy of formation of a gaseous species i which is taken from Prausnitz et al. (1980) (see Table 11). The temperature-dependent molar heat capacities $c_{\mathrm{p},i,\mathrm{id.gas}}$ are taken from Riedel (1974; see Table 11). The fugacity coefficients are

Table 11. Standard Enthalpies of Formation (Riedel, 1974) and Molal Heat Capacities (Prausnitz et al., 1980) of Ammonia, Carbon Dioxide, and Water in the Ideal Gas State

$$\frac{c_{\mathrm{p},i,\mathrm{id.gas}}}{\mathrm{J/(mol{\cdot}K)}} = A_i + \frac{B_i}{(T/\mathrm{K})} + C_i(T/\mathrm{K}) + D_i \ln(T/\mathrm{K})$$

i	$h_i^{\ominus}(T^{\ominus})$, kJ/mol	A_i	B_i	C_i	D_i
NH_3	−46.19	−87.547	4098.5	1.172×10^{-2}	18.583
CO_2	−393.51	−109.19	2466.3	-9.7531×10^{-3}	24.740
H_2O	−241.8	25.573	897.86	1.3705×10^{-2}	0.15825

calculated from the virial equation of state truncated after the second virial coefficient:

$$\ln \varphi_{i,\mathrm{gas}}(T,p,y_j) = (2\sum_j y_j B_{i,j} - B_{\mathrm{mix}})\frac{p}{RT} \tag{29}$$

where

$$B_{\mathrm{mix}} = \sum_i \sum_j y_i y_j B_{i,j} \tag{30}$$

Thus, the residual part of the molar enthalpy of the gaseous mixture is

$$\delta h_{\mathrm{mix}}(T,p,y_j) = \sum_i y_i h_{i,\mathrm{id.gas}}(T) + \left(B_{\mathrm{mix}} - T\left(\frac{\partial B_{\mathrm{mix}}}{\partial T}\right)_{p,y_j}\right)p \tag{31}$$

Pure component second virial coefficients $B_{i,i}$ are calculated from correlations based on the data given by Dymond and Smith (1980; see Table 3), whereas mixed second virial coefficients are calculated according to the method by Hayden and O'Connell (1975).

2. Partial Molar Enthalpies of Dissolved Species and Solvent Water. Enthalpy of Pure Liquid Water. The enthalpy of pure liquid water at temperature T and pressure p is calculated from the partial molar enthalpy of gaseous pure water:

$$h_{\mathrm{w}}(T,p)_{\mathrm{liq,pure}} = h_{\mathrm{w}}(T)^{\mathrm{pure}}_{\mathrm{id.\ gas}} + \left(B_{\mathrm{w,w}} - T\left(\frac{\partial B_{\mathrm{w,w}}}{\partial T}\right)_p\right)p^{\mathrm{s}}_{\mathrm{w}} - \Delta h^{\mathrm{v}}_{\mathrm{w}}(T) + \Delta h^{\mathrm{liq}}_{\mathrm{w}}(T,\ p^{\mathrm{s}}_{\mathrm{w}} \rightarrow p) \tag{32}$$

where $\Delta h^{\mathrm{v}}_{\mathrm{w}}(T)$ is the enthalpy of evaporization of water that is calculated from the equations by Saul and Wagner (1987). The last term describing the influence of pressure on the enthalpy of pure liquid water is neglected.

Reference Enthalpy of a Dissolved Species *i*. To calculate the reference enthalpy h_i^{∞} of a dissolved species i, the reference enthalpy of hydrogen ions is set to zero at all temperatures:

$$h^{\infty}_{\mathrm{H^+,w}}(T) = 0 \tag{33}$$

The pressure dependence on the reference enthalpy of a dissolved species i is neglected. The temperature-dependent partial molar enthalpies were then calculated from the temperature-dependent equilibrium constants for reactions I−V (see Table 1):

$$h^{\infty}_{\mathrm{OH^-,w}}(T) = h_{\mathrm{w}}(T)_{\mathrm{liq,pure}} + RT^2\left(\frac{\partial \ln K_{\mathrm{V}}(T)}{\partial T}\right) \tag{34}$$

$$h^{\infty}_{\mathrm{NH_4^+,w}}(T) = h^{\infty}_{\mathrm{NH_3,w}}(T) + h_{\mathrm{w}}(T)_{\mathrm{liq,pure}} - h^{\infty}_{\mathrm{OH^-,w}}(T) + RT^2\left(\frac{\partial \ln K_{\mathrm{I}}(T)}{\partial T}\right) \tag{35}$$

$$h^{\infty}_{\mathrm{HCO_3^-,w}}(T) = h^{\infty}_{\mathrm{CO_2,w}}(T) + h_{\mathrm{w}}(T)_{\mathrm{liq,pure}} + RT^2\left(\frac{\partial \ln K_{\mathrm{II}}(T)}{\partial T}\right) \tag{36}$$

$$h^{\infty}_{\mathrm{CO_3^{2-},w}}(T) = h^{\infty}_{\mathrm{HCO_3^-,w}}(T) + RT^2\left(\frac{\partial \ln K_{\mathrm{III}}(T)}{\partial T}\right) \tag{37}$$

$$h^{\infty}_{\mathrm{NH_2COO^-,w}}(T) = h^{\infty}_{\mathrm{NH_3,w}}(T) + h^{\infty}_{\mathrm{HCO_3^-,w}}(T) - h_{\mathrm{w}}(T)_{\mathrm{liq,pure}} + RT^2\left(\frac{\partial \ln K_{\mathrm{IV}}(T)}{\partial T}\right) \tag{38}$$

The equations just presented require the partial molar enthalpies of ammonia and carbon dioxide dissolved in water at infinite dilution, which were calculated from the temperature dependence of Henry's constants (see Table 2):

$$h^{\infty}_{i,\mathrm{w}}(T) = h_{i,\mathrm{id.gas}}(T) - RT^2\left(\frac{\partial \ln(H^{(\mathrm{m})}_{i,\mathrm{w}}(T,p^{\mathrm{s}}_{\mathrm{w}})/(p^{\ominus}/m^{\ominus}))}{\partial T}\right) \quad i = \mathrm{NH_3,\ CO_2} \tag{39}$$

where $h_{i,\mathrm{id.gas}}(T)$ was calculated from eq 28.

Partial Molar Excess Enthalpies. The partial molar excess enthalpy h_i^{E} of a species i can be calculated from the model for the excess Gibbs energy of the solution by applying eq 20. By applying that equation to the Pitzer model, it can be seen that the partial molar enthalpies can be calculated by replacing the temperature-dependent interaction parameters and the Debye−Hückel parameter in the equations for the activity coefficient of a species i and the activity of water (see, for example, Bieling et al. (1995)) according to the following scheme:

$$A_{\phi}\text{: replace by } \partial A_{\phi}/\partial T \tag{40}$$

$$\beta^{(0)}_{i,j}\text{: replace by } \partial\beta^{(0)}_{i,j}/\partial T \tag{41}$$

$$\beta^{(1)}_{i,j}\text{: replace by } \partial\beta^{(1)}_{i,j}/\partial T \tag{42}$$

$$\tau_{i,j,k}\text{: replace by } \partial\tau_{i,j,k}/\partial T \tag{43}$$

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