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Enthalpy of mixing of aqueous solutions of NH_3 with aqueous solutions of Na_2SO_4 or $(NH_4)_2SO_4$ at temperatures between 313 and 373 K

Frank Weyrich, Bernd Rumpf, Gerd Maurer*

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

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Abstract

The enthalpy of mixing (at constant temperature and pressure) an aqueous solution of ammonia with an aqueous solution of either sodium sulfate or ammonium sulfate was measured by batch calorimetry at temperatures from 313 to 373 K. The experimental results are, first, used for comparison with predictions from a modified Pitzer's model for the solubility of ammonia in aqueous solutions of those strong electrolytes and, secondly, to tune the influence of temperature on some parameters of that model. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Calorimetry; Electrolyte solutions; Ammonia; Sulfates

1. Introduction

The present contribution continues a series of publications on the thermodynamic properties of aqueous solutions of ammonia [1–3] which are part of an extensive study on the solubility (and related phenomena) of ammonia and a sour gas — e.g. carbon dioxide, sulfur dioxide or hydrogen sulfide — in water and in aqueous solutions [4–13]. Such gas solubility data were correlated applying an extension of Pitzer's method [14] for the Gibbs excess energy of an aqueous phase. This method requires binary and ternary interaction parameters between solute species. The interaction parameters depend on temperature. However, it is often difficult to determine the influence of vapor–liquid equilibrium data alone. But that influence can be revealed in calorimetric experiments, e.g. in measuring the change of enthalpy observed when an aqueous solution of ammonia is mixed at constant temperature and pressure with an aqueous solution of a strong electrolyte. Therefore, such measurements were performed. The results are used for comparisons with predictions derived from a model for the solubility of ammonia in aqueous solutions of strong electrolytes. Furthermore, the results are used to adjust the influence of temperature on model parameters.

This contribution reports new experimental data for the enthalpy change observed when an aqueous solution of ammonia is mixed with an aqueous solution of either sodium sulfate or ammonium sulfate at constant (and low) pressure and temperatures between about 313 and 373 K. The molality of ammonia in the solution (before mixing) was either 6 or 12 mol/kg of water, the salt molality was varied from 0.5 to 1.5

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* Corresponding author. Tel.: +49-631-205-2410;
fax: +49-631-205-3835.
E-mail address: gmaurer@rhrk.uni-kl.de (G. Maurer)

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molal and from 1 to 5 molal for sodium sulfate and ammonium sulfate, respectively.

2. Experimental

The experimental arrangement is the same as that used in a previous investigation [2]. Therefore, only a short description is given here. In an experiment, two identical pressurized mixing cells were placed into a Calvet-type batch calorimeter (MS 70, SETARAM, Lyon, France). One cell was used as reference in a differential arrangement, the other for the actual experiment. Each cell contained two liquid samples in an upper and lower compartment, respectively. The compartments were separated by a thin teflon foil. The upper compartment was filled with an aqueous solution of ammonia, the lower compartment with an aqueous solution of either Na_2SO_4 or $(NH_4)_2SO_4$. In a typical experiment about 25 g of an aqueous solution of ammonia was in the upper compartment of a mixing cell, whereas about 18 g of an aqueous solution of either Na_2SO_4 or $(NH_4)_2SO_4$ was in the lower cell. The samples were prepared as described in [2]. The mass of a solution in a compartment is known with a maximum uncertainty of ±0.08 g. The molality of a solute in an aqueous solution is known within ±0.3%. The temperature in the batch calorimeter was determined by calibrated platinum resistance thermometers. The uncertainty of the temperature is smaller than ±0.1 K. After thermal equilibration in the batch calorimeter the teflon foil separating both compartments in a cell was cut and the solutions mixed. The calorimeter response was determined, converted to the experimental heat of mixing (using calibration curves) and corrected for the energy involved in the cutting process (cf. [2]). For reliable experimental results it is particularly important to avoid a vapor phase in the cells during an experiment. Therefore, the cells were pressurized as described in detail before [2] applying a constant pressure between about 0.5 and 1 MPa by a flexible bellows. While the pressure inside that bellows was kept constant and above the saturation pressure of each of the aqueous solutions, the pressure on the outer side of the bellows (i.e. of the liquid solutions inside the mixing cells) can slightly change due to an compression/extension of the bellows which again is caused by a volume change on mixing the aqueous phases. Therefore, the enthalpy of mixing ΔH_{mix}, has to be calculated from the experimental results for the heat of mixing, Q_{mix}, applying a small correction $\delta(\Delta H_{\mathrm{mix}})$:

$$\Delta H_{\mathrm{mix}} = Q_{\mathrm{mix}} + \delta(\Delta H_{\mathrm{mix}}) \tag{1}$$

That correction can only be calculated when information on the density of the aqueous solutions is available [2]. As that information is not available, the correction had to be neglected:

$$\Delta H_{\mathrm{mix}} \approx Q_{\mathrm{mix}} \tag{2}$$

However, from investigations of similar systems (NH_3+H_2O, $Na_2SO_4+H_2O$, and $(NH_4)_2SO_4+H_2O$) it is known that the correction is smaller than 1 J. Including all other experimental uncertainties (e.g. uncertainties from calibrating the calorimeter response, the amount of substances in the compartments etc.), the total uncertainty of the experimental data for the enthalpy of mixing is estimated to be ±2 J.

3. Substances

Ammonia (≥99.999 mol%) was purchased from Messer-Griesheim, Ludwigshafen a. Rh., Germany and used without further treatment. Sodium sulfate (≥99 mass%) and ammonium sulfate (≥99.5 mass%) were purchased from Merck, Darmstadt, Germany. Both salts were degassed and tried under vacuum. Deionized and vacuum distilled water was used in all experiments.

4. Results

The experimental results for the enthalpy of mixing are given in Tables 1 and 2. The tables provide numerical results for the temperature, the molality of ammonia in the aqueous mixture in the upper compartment and of the salt in the lower compartment of a mixing cell both before mixing, the masses of the solutions in both compartments and the experimental result for the enthalpy of mixing. As the total pressure has only a very small influence on the experiments, no pressure data are reported. The results are also shown in Figs. 1 and 2 together with some data for the dilution of aqueous systems of ammonia with pure

Table 1
Experimental results for the enthalpy of mixing of aqueous solutions of ammonia with aqueous solutions of sodium sulfate

T (K)	$m_{\mathrm{NH_3}}^{(\mathrm{upper})}$	$m_{\mathrm{Na_2SO_4}}^{(\mathrm{lower})}$ (g)	$\tilde{m}^{(\mathrm{upper})}$ (g)	$\tilde{m}^{(\mathrm{lower})}$ (g)	ΔH_{mix} (J)
313.15±0.05	6.017	0.500	26.889	16.929	9.9
		0.500	27.143	16.903	9.1
		1.000	27.204	17.829	60.6
		1.000	27.070	17.832	59.9
		1.500	26.028	18.707	113.3
		1.500	26.649	18.695	112.8
313.15±0.05	12.01	0.500	25.826	16.921	−61.7
		0.500	25.823	16.792	−60.9
		1.000	25.239	17.888	18.6
		1.000	24.912	17.836	17.7
		1.500	26.294	18.718	101.7
		1.500	26.151	18.683	100.0
333.45±0.05	6.266	0.500	26.510	16.870	−0.5
		0.500	25.948	16.902	−1.0
		1.000	26.826	17.909	35.9
		1.000	26.805	17.846	35.8
		1.500	26.429	18.705	75.2
		1.500	25.872	18.760	75.5
333.05±0.05	11.94	0.500	26.408	16.929	−67.6
		0.500	26.518	16.850	−67.9
	12.07	1.012	24.552	17.572	−1.1
		1.012	24.265	17.609	1.1
	11.94	1.500	26.422	18.574	64.3
		1.500	26.281	18.529	63.7
353.1±0.1	6.041	0.500	26.114	16.912	−10.1
		0.500	26.061	16.870	−10.5
		1.000	24.375	17.755	12.4
		1.000	24.479	17.744	12.7
	5.957	1.500	26.040	18.539	36.0
		1.500	25.961	18.509	36.6
353.1±0.1	11.97	0.500	25.669	16.965	−84.3
		0.500	25.120	16.927	−83.9
	12.13	1.000	24.122	17.697	−33.5
	11.90	1.000	25.555	17.742	−30.8
		1.000	24.058	17.729	−30.9
	11.97	1.500	25.280	18.666	20.0
		1.500	25.114	18.581	20.3
373.35±0.05	6.167	0.500	23.870	16.578	−20.2
		0.500	23.998	15.604	−20.8
		1.000	25.561	17.390	−10.9
		1.000	25.415	17.422	−10.4
		1.500	23.798	18.241	−0.8
		1.500	24.009	18.263	−0.7
373.35±0.05	11.96	0.500	22.899	16.570	−89.3
		0.500	22.072	16.521	−89.1
		1.000	25.083	17.058	−59.9
		1.000	24.687	17.319	−59.3
		1.500	24.666	18.247	−32.2
		1.500	24.658	18.157	−32.1

Table 2
Experimental results for the enthalpy of mixing of aqueous solutions of ammonia with aqueous solutions of ammonium sulfate

T (K)	$m_{\mathrm{NH_3}}^{(\mathrm{upper})}$	$m_{\mathrm{(NH_4)_2SO_4}}^{(\mathrm{lower})}$ (g)	$\tilde{m}^{(\mathrm{upper})}$ (g)	$\tilde{m}^{(\mathrm{lower})}$ (g)	ΔH_{mix} (J)
313.15±0.05	5.947	0.998	25.862	17.065	1.0
		0.998	25.498	17.105	1.2
		3.004	25.969	18.500	52.7
		3.004	25.667	18.669	53.1
		4.985	26.210	19.649	60.1
		4.985	25.758	19.601	58.3
		4.985	25.377	19.639	57.8
313.15±0.05	12.22	0.998	25.651	17.161	−64.8
		0.998	25.466	16.781	−64.6
		3.004	24.897	18.231	23.7
		3.004	26.090	18.904	23.7
		4.985	25.589	19.664	61.6
		4.985	25.496	19.629	61.5
333.25±0.05	6.203	1.003	25.867	16.955	−12.4
		1.003	25.461	17.085	−12.3
		3.021	25.584	18.629	1.6
		3.021	24.791	18.549	1.8
		5.019	24.925	19.604	−25.8
		5.019	25.105	19.674	−25.6
333.05±0.05	11.94	1.000	25.421	16.972	−81.5
		1.000	25.408	16.932	−82.0
		2.000	26.248	17.749	−48.7
		2.000	26.198	17.883	−48.6
		2.000	26.284	17.827	−49.2
		3.000	25.591	18.530	−25.7
		3.000	25.418	18.550	−24.8
333.30±0.05	12.02	5.019	24.767	19.724	−20.5
		5.019	24.453	19.677	−21.0
353.1±0.1	6.050	1.008	25.006	17.060	−26.8
		1.008	25.106	17.033	−26.7
		3.033	24.909	18.494	−51.7
		3.033	24.448	18.586	−51.2
		4.996	25.415	19.522	−111.6
		4.996	25.790	19.517	−112.8
353.1±0.1	12.02	1.003	23.820	17.073	−101.1
		1.003	24.149	17.017	−101.5
		1.003	23.483	17.065	−100.4
		3.019	24.249	18.437	−82.9
		3.019	24.143	18.473	−81.5
		4.999	24.354	19.595	−111.6
		4.999	25.229	19.595	−114.0
373.30±0.1	5.794	0.994	24.538	16.614	−41.9
		0.994	24.447	16.600	−42.6
		3.001	25.655	18.147	−100.5
		3.001	25.647	18.232	−102.3
		5.013	24.330	19.291	−194.5
		5.013	24.462	19.261	−195.2
	12.14	0.994	24.963	16.653	−120.1
		0.994	23.413	16.563	−118.0

Table 2 (*Continued*)

T (K)	$m_{\mathrm{NH_3}}^{(\mathrm{upper})}$	$m_{\mathrm{(NH_4)_2SO_4}}^{(\mathrm{lower})}$ (g)	$\tilde{m}^{(\mathrm{upper})}$ (g)	$\tilde{m}^{(\mathrm{lower})}$ (g)	ΔH_{mix} (J)
		3.001	24.719	18.153	−136.9
		3.001	24.691	18.257	−139.8
		5.013	24.600	19.122	−204.3
		5.013	24.489	19.226	−204.8

water which were published before [2]. When an aqueous solution of ammonia is diluted with pure water at constant temperature and (low) pressure the enthalpy of mixing is negative. The addition of Na_2SO_4 to the aqueous phase which is mixed with the aqueous solution of ammonia increases the enthalpy of mixing, resulting even in a positive enthalpy of mixing at sufficient large salt molalities. Temperature has only little influence on the enthalpy of mixing when pure water is the diluent, but with increasing salt molality the influence of temperature increases, particularly at low temperatures. When ammonium sulfate (instead of Na_2SO_4) is added to the aqueous phase which is mixed with the aqueous solution of ammonia the enthalpy of mixing increases with increasing salt concentration only at lower temperatures (e.g. at 313 K), whereas it decreases at higher temperatures (e.g. at 373 K). Thus, at intermediate temperatures (e.g. at 333 K) the enthalpy of mixing runs through a maximum.

4.1. Modeling

The model of Pitzer [14] is applied to describe the Gibbs excess energy G^{E} of the aqueous solution:

$$\frac{1000G^{\mathrm{E}}}{n_{\mathrm{w}}RTM_{\mathrm{w}}} = f(I_{\mathrm{m}}) + \sum_{i\neq \mathrm{w}}\sum_{j\neq \mathrm{w}} m_i m_j \lambda_{i,j}(I_{\mathrm{m}}) + \sum_{i\neq \mathrm{w}}\sum_{j\neq \mathrm{w}}\sum_{k\neq \mathrm{w}} m_i m_j m_k \tau_{i,j,k}. \tag{3}$$

$f(I_{\mathrm{m}})$ is a modified Debye–Hückel contribution:

$$f(I_{\mathrm{m}}) = -A_{\varphi}\frac{4I_{\mathrm{m}}}{b}\ln(1 + b\sqrt{I_{\mathrm{m}}}) \tag{4}$$

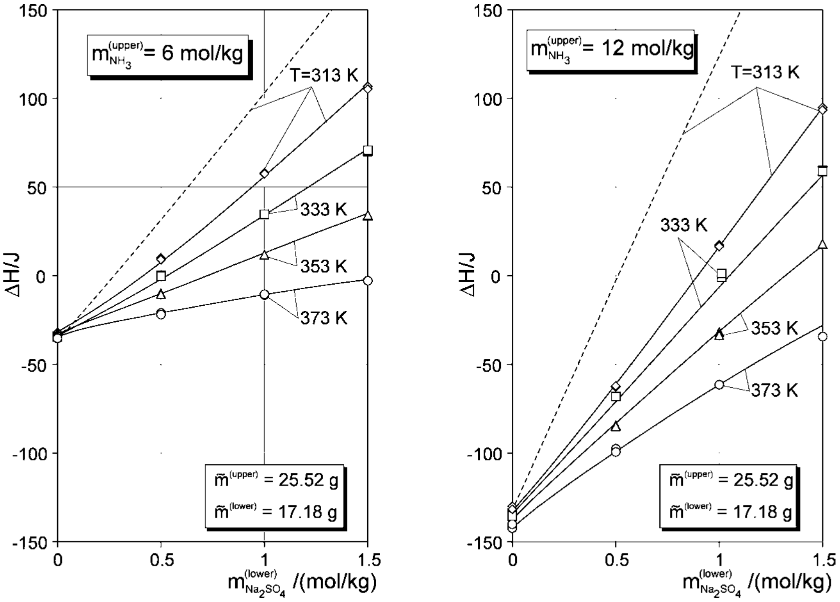

Fig. 1. Change of enthalpy on the isothermal and isobaric mixing of an aqueous solution of NH_3 (superscript (o)) with an aqueous solution of Na_2SO_4 (superscript (u)); ○, △, □, ◇: experimental, this work; - - -: prediction; —: correlation.

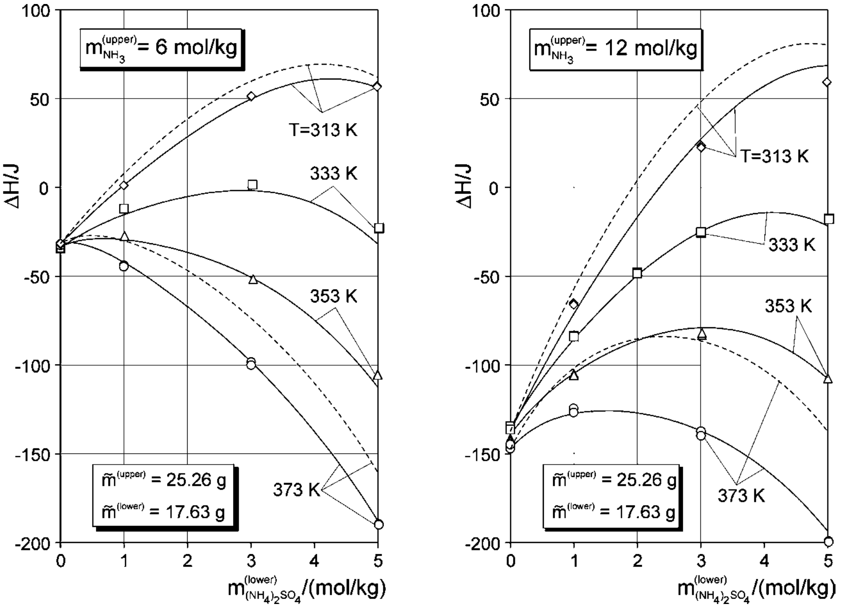

Fig. 2. Change of enthalpy on the isothermal and isobaric mixing of an aqueous solution of NH_3 (superscript (o)) with an aqueous solution of $(NH_4)_2SO_4$ (superscript (u)); ○, △, □, ◇: experimental results, this work; - - -: prediction; —: correlation.

where b denotes a constant (b=1.2 (mol/kg $H_2O)^{-1/2}$) and I_m is the ionic strength:

$$I_{\mathrm{m}} = \frac{1}{2}\sum_i z_i^2 m_i \tag{5}$$

A_φ is the Debye–Hückel parameter:

$$A_\varphi = \frac{1}{3}\sqrt{2\pi N_{\mathrm{A}}\rho_{\mathrm{w,liq}}^{\mathrm{s}}}\left(\frac{e^2}{4\pi\varepsilon_0\varepsilon_{\mathrm{w}}kT}\right)^{1.5} \tag{6}$$

The second virial coefficient $\lambda_{i,j}$ depends on the ionic strength:

$$\lambda_{i,j}(I_{\mathrm{m}}) = \beta_{i,j}^{(0)} + \frac{2}{\alpha^2 I_{\mathrm{m}}}\beta_{i,j}^{(1)} \times [1-(1+\alpha\sqrt{I_{\mathrm{m}}})\exp(-\alpha\sqrt{I_{\mathrm{m}}})]. \tag{7}$$

As recommended by Pitzer [14], parameter α is set to α=2.0 for 1:1 and 2:1 electrolytes.

$\beta_{ij}^{(0)}$, $\beta_{ij}^{(1)}$ and τ_{ijk} are binary and ternary interaction parameters which might depend on temperature. As usual, it is assumed that those parameters are symmetric:

$$\beta_{i,j}^{(0)} = \beta_{j,i}^{(0)} \tag{8}$$

$$\beta_{i,j}^{(1)} = \beta_{j,i}^{(1)} \tag{9}$$

$$\tau_{i,j,k} = \tau_{i,k,j} = \tau_{j,i,k} = \tau_{j,k,i} = \tau_{k,i,j} = \tau_{k,j,i} \tag{10}$$

Furthermore, it is common practice to neglect all parameters between ionic species carrying either only positive or only negative charges.

For aqueous solutions of a single strong electrolyte $M_{\nu_+}X_{\nu_-}$ one cannot separate the influence of the remaining ternary parameters $\tau_{M,M,X}$ and $\tau_{M,X,X}$. Therefore, it is also common to set one of those parameters to zero, e.g. $\tau_{M,X,X}$, and to describe the influence of ternary interactions between the ions only by $\tau_{M,M,X}$. Furthermore it is also common practice to replace that parameter by the third osmotic virial coefficient C^Φ. For a 2:1 electrolyte the following relation holds between $\tau_{M,M,X}$ and $C_{M_2X}^\Phi$:

$$\tau_{\mathrm{M,M,X}} = \frac{\sqrt{2}}{6}C_{\mathrm{M_2X}}^{\Phi} \tag{11}$$

where i represents a neutral solute G, j and k stand for a cation M and anion X of a strong electrolyte $M_{\nu_+}X_{\nu_-}$, the influence of M and X on the solute G cannot be separated, and therefore, it is common practice to combine parameters $\beta_{G,M}^{(0)}$ and $\beta_{G,X}^{(0)}$ in a single binary parameter $B_{G,MX}^{(0)}$:

$$B_{\mathrm{G,MX}}^{(0)} = \nu_+\beta_{\mathrm{G,M}}^{(0)} + \nu_-\beta_{\mathrm{G,X}}^{(0)} \tag{12}$$

For similar reasons ternary parameters for interactions between that solute G and the strong electrolyte, $\tau_{G,j,k}$ where i and j represent M and X, are comprehended to two ternary parameters $\Gamma_{G,MX,MX}$ and $\Gamma_{G,G,MX}$:

$$\Gamma_{G,MX,MX} = \nu_+^2 \tau_{G,M,M} + 2\nu_+\nu_- \tau_{G,M,X} + \nu_-^2 \tau_{G,X,X} \tag{13}$$

$$\Gamma_{G,G,MX} = \nu_+ \tau_{G,G,M} + \nu_- \tau_{G,G,X} \tag{14}$$

The partial molar excess enthalpies of ammonia, water and either sodium or ammonium sulfate are calculated from the Gibbs excess energy using standard thermodynamics. The excess enthalpy of the aqueous mixture is the sum of contributions from all components. As the concentration of ammonia in the aqueous phases is comparatively high, both the autoprotolysis of water and the protonation of ammonia can be neglected. The final result for the enthalpy change when an aqueous solution of ammonia is mixed at constant temperature and pressure with an aqueous solution of an 2:1 electrolyte (M_2X) can be written as follows [18]:

$$+\Delta H_{\mathrm{mix}} = \Delta H_{(NH_3+H_2O)} + \Delta H_{(M_2X+H_2O)} + \Delta H_{(NH_3\leftrightarrow M_2X)} \tag{15}$$

$\Delta H_{(NH_3+H_2O)}$ is the contribution from diluting the aqueous solution of ammonia with pure water:

$$\begin{aligned}\frac{-\Delta H_{(NH_3+H_2O)}}{RT^2} &= +\tilde{n}_{NH_3}\frac{\partial}{\partial T}[\ln\gamma_{NH_3}^{(m)}(T, m_{NH_3}^{(2)}) \\ &\quad - \ln\gamma_{NH_3}^{(m)}(T, m_{NH_3}^{(\mathrm{upper})})] + \tilde{n}_{w}^{(\mathrm{upper})}\frac{\partial}{\partial T} \\ &\quad \times [\ln a_w(T, m_{NH_3}^{(2)}) - \ln a_w(T, m_{NH_3}^{(\mathrm{upper})})] \\ &\quad + \tilde{n}_w^{(\mathrm{lower})}\frac{\partial}{\partial T}[\ln a_w(T, m_{NH_3}^{(2)})]\end{aligned} \tag{15a}$$

$\Delta H_{(M_2X+H_2O)}$ is the contribution from diluting the aqueous solution of strong electrolyte M_2X with pure water:

$$\begin{aligned}\frac{-\Delta H_{(M_2X+H_2O)}}{RT^2} &= 3\tilde{n}_{M_2X}\frac{\partial}{\partial T}[\ln\gamma_{M_2X}^{\pm,(m)}(T, m_{M_2X}^{(2)}) \\ &\quad - \ln\gamma_{M_2X}^{\pm,(m)}(T, m_{M_2X}^{(\mathrm{lower})})] + \tilde{n}_w^{(\mathrm{lower})}\frac{\partial}{\partial T} \\ &\quad \times [\ln a_w(T, m_{M_2X}^{(2)}) - \ln a_w(T, m_{M_2X}^{(\mathrm{lower})})] \\ &\quad + \tilde{n}_w^{(\mathrm{upper})}\frac{\partial}{\partial T}[\ln a_w(T, m_{M_2X}^{(2)})]\end{aligned} \tag{15b}$$

where

$$\ln\gamma_{M_2X}^{\pm,(m)} = \tfrac{1}{3}(2\ln\gamma_M^{(m)} + \ln\gamma_X^{(m)}) \tag{15c}$$

$\Delta H_{(NH_3\leftrightarrow M_2X)}$ is the contribution resulting from interactions between ammonia and the strong electrolyte M_2X in the solution after mixing:

$$\begin{aligned}\frac{-\Delta H_{(NH_3\leftrightarrow M_2X)}}{RT^2} &= m_{NH_3}^{(2)} \times m_{M_2X}^{(2)}\frac{\partial}{\partial T}\Bigg[2\tilde{n}_w\frac{M_w}{1000}B_{NH_3,M_2X}^{(0)} \\ &\quad + 3\tilde{n}_{NH_3}\Gamma_{NH_3,NH_3,M_2X} + 3\tilde{n}_{M_2X}\Gamma_{NH_3,M_2X,M_2X}\Bigg]\end{aligned} \tag{15d}$$

The expressions for the activity coefficients $\gamma_i^{(m)}$ (i=M, X, NH_3) and for the activity of water a_w are given in Appendix A.

4.2. Model parameters

The following properties are required for predicting the enthalpy of mixing:

- The dielectric constant of water ε_w. It was taken from [15]. The influence of pressure on ε_w was approximated by replacing the pressure by the saturation pressure of pure water.
- The density of saturated liquid water, $\rho_{w,\mathrm{liq}}^{s}$, which was taken from [16].
- Binary and ternary interaction parameters for $Na_2SO_4+H_2O$ ($\beta^{(0)}_{Na^+,SO_4^{2-}}$, $\beta^{(1)}_{Na^+,SO_4^{2-}}$ and $\tau_{Na^+,Na^+,SO_4^{2-}} (= (\sqrt{2}/6)C^{\Phi}_{Na_2SO_4})$) were taken from [17].
- Binary and ternary interaction parameters for $(NH_4)_2SO_4+H_2O$ ($\beta^{(0)}_{NH_4^+,SO_4^{2-}}$, $\beta^{(1)}_{NH_4^+,SO_4^{2-}}$ and $\tau_{NH_4^+,NH_4^+,SO_4^{2-}} (= (\sqrt{2}/6)C^{\Phi}_{(NH_4)_2SO_4})$) were taken from [2].
- Binary and ternary interaction parameters for NH_3+H_2O ($\beta^{(0)}_{NH_3,NH_3}$ and τ_{NH_3,NH_3,NH_3}) were also taken from [2].
- Binary and ternary parameters for interactions between ammonia and sodium sulfate ($B^{(0)}_{NH_3,Na_2SO_4}$, $\Gamma_{NH_3,Na_2SO_4,Na_2SO_4}$) and between ammonia and ammonium sulfate ($B^{(0)}_{NH_3,(NH_4)_2SO_4}$, $\Gamma_{NH_3,(NH_4)_2SO_4,(NH_4)_2SO_4}$ and $\Gamma_{NH_3,NH_3,(NH_4)_2SO_4}$) as determined from experimental data for the solubi-

lity of ammonia in aqueous solutions of sodium and ammonium sulfate by Rumpf and Maurer [1] were adopted.

When this set of parameters is used for the calculation of the vapor–liquid equilibrium, the results are designated by ‘former correlation’.

5. Comparison of the new experimental data with the prediction and correlation

With these parameters the enthalpy of mixing can be calculated. The results of such calculations for the enthalpy of mixing are here called ‘predictions’. Figs. 1 and 2 show some selected, but typical comparisons of experimental data with predictions. As in a series of experiments neither the solute molality nor the masses of the solutions in the compartments of a mixing cell could be kept constant, the calculations were performed with ‘averaged’ numbers for those properties. These numbers are also given in Figs. 1 and 2. The prediction overestimates the enthalpy of mixing, i.e. predicted enthalpies of mixing are larger than the experimental results. The contributions to ΔH_{mix} caused by diluting the aqueous solution of ammonia with water ($\Delta H_{(\mathrm{NH_3+H_2O})}$; cf. Eq. (15)) and those caused by diluting the aqueous solution of a salt by water ($\Delta H_{(\mathrm{M_2X+H_2O})}$; cf. Eq. (15)) were calculated using a set of interaction parameters given in [2]. Some typical results are given in Tables 3 and 4 (for Na_2SO_4 and $(NH_4)_2SO_4$, respectively). $\Delta H_{(\mathrm{NH_3+H_2O})}$ is always negative. It increases with increasing concentration of ammonia in the aqueous phase as well as with increasing temperature. $\Delta H_{(\mathrm{Na_2SO_4+H_2O})}$ is positive at low temperatures and negative at high temperatures. The absolute number for $\Delta H_{(\mathrm{Na_2SO_4+H_2O})}$ increases with increasing salt molality. $\Delta H_{(\mathrm{(NH_4)_2SO_4+H_2O})}$ is predominantly negative. The absolute number for $\Delta H_{(\mathrm{(NH_4)_2SO_4+H_2O})}$ increases with increasing salt molality. However, in all experiments the contribution $\Delta H_{(\mathrm{NH_3\leftrightarrow M_2X})}$ to ΔH_{mix} is of the same order of magnitude as both other contributions, but it is always positive. Thus, the influence of interactions between ammonia and a salt on ΔH_{mix} in such aqueous solutions is large and small uncertainties in the influence of the interaction parameters between ammonia and the ionic species result in a large uncertainty in the predictions for the enthalpy of mixing. The parameters had been determined from gas solubility data alone [1]. Those parameters were, therefore, adjusted using the gas solubility data as well as the new calorimetric results. Results from calculations with that new parameter set are designated as ‘new correlation’. Details of the calculation of the vapor–liquid equilibrium are given in Appendix A. The results are given in Tables 5 and 6. Figs. 1 and 2 also show a comparison of the experimental data for the enthalpy of mixing with the new correlation. The average/maximum absolute deviation between the experimental data and the new correlation is 1.5/6 J (for $NH_3+Na_2SO_4+H_2O$) and 2.8/10 J (for $NH_3+(NH_4)_2SO_4+H_2O$). A comparison with experimental results for the solubility of ammonia in an aqueous solution of either sodium sulfate or ammonium sulfate is shown in Figs. 3 and 4. The new correlation represents the experimental results for

Table 3
Calculated contributions to the enthalpy of mixing when 25.52 g of an aqueous solution of ammonia are mixed at constant temperature and (low) pressure with 17.18 g of an aqueous solution of sodium sulfate (parameters for interactions between ammonia and sodium sulfate from Table 5)

T (K)	$m_{\mathrm{NH_3}}^{(\mathrm{upper})}$	$m_{\mathrm{Na_2SO_4}}^{(\mathrm{lower})}$	$\Delta H_{(\mathrm{NH_3+H_2O})}$ (J)	$\Delta H_{(\mathrm{Na_2SO_4+H_2O})}$ (J)	$\Delta H_{(\mathrm{NH_3\leftrightarrow Na_2SO_4})}$ (J)	ΔH_{mix} (J)
313.15	6.0	0.5	−30.4	3.8	34.0	7.4
		1.5	−28.3	42.2	93.8	107.7
	12.0	0.5	−126.5	3.7	62.7	−60.1
		1.5	−118.0	40.7	172.5	95.2
373.15	6.0	0.5	−31.8	−19.1	30.7	−20.2
		1.5	−29.6	−57.1	84.5	−2.2
	12.0	0.5	−137.1	−18.1	56.2	−99.0
		1.5	−128.0	−54.00	154.5	−27.5

Table 4
Calculated contributions to the enthalpy of mixing when 25.26 g of an aqueous solution of ammonia are mixed at constant temperature and (low) pressure with 17.63 g of an aqueous solution of ammonium sulfate (parameters for interactions between ammonia and ammonium sulfate from Table 6)

T (K)	$m_{NH_3}^{(upper)}$	$m_{(NH_4)_2SO_4}^{(lower)}$	$\Delta H_{(NH_3+H_2O)}$ (J)	$\Delta H_{((NH_4)_2SO_4+H_2O)}$ (J)	$\Delta H_{(NH_3 \leftrightarrow (NH_4)_2SO_4)}$ (J)	ΔH_{mix} (J)
313.15	6.0	1.0	−29.8	0.4	30.4	0.9
		5.0	−23.4	−28.2	108.1	56.0
	12.0	1.0	−123.9	0.4	56.0	−67.7
		5.0	−98.5	−28.4	196.8	69.1
373.15	6.0	1.0	−31.2	−36.5	24.5	−43.2
		5.0	−24.5	−246.4	84.8	−186.1
	12.0	1.0	−134.3	−34.6	44.6	−124.3
		5.0	−107.2	−236.1	151.6	−191.7

Table 5
Readjusted binary and ternary parameters for interactions between ammonia and sodium sulfate in aqueous solutions at temperatures between 313 and 433 K[a]

	A	B	C	D
$B_{NH_3,Na_2SO_4}^{(0)}$	0.662878	–	−0.223236	0.023290
$\Gamma_{NH_3,NH_3,Na_2SO_4}$	0.87709×10^{-3}	−0.662155	–	–
$\Gamma_{NH_3,Na_2SO_4,Na_2SO_4}$	0.252274×10^{-4}	−0.977201	–	–

[a] $f(T) = A + (B/T) + C(T/100) + D(T/100)^2$; $f \equiv (B_{NH_3,Na_2SO_4}^{(0)}, \Gamma_{NH_3,NH_3,Na_2SO_4}, \Gamma_{NH_3,Na_2SO_4,Na_2SO_4})$.

the total pressure above an aqueous solution of ammonia and sodium sulfate of Rumpf and Maurer [1] (in two-phase, i.e. vapor and liquid — but also in the three-phase, i.e. vapor, liquid and solid region) nearly as reliable as the former correlation, which was based on gas solubility data alone. For example, at 433 K the mean relative deviation in the total pressure

$$|\Delta p/p| = \frac{1}{N_{exp}} \sum_{i=1}^{N_{exp}} \frac{|p_{exp} - p_{calc}|_i}{p_{exp,i}} \qquad (16)$$

is 0.56% with the new correlation, whereas it is 0.50% for the former correlation. The pressure decreases when the temperature drops (at constant molality of ammonia and sodium sulfate) and consequently the experimental uncertainty increases. This is also reflected in larger deviations between the experimental result for the total pressure and the calculation, e.g. at 333 K the mean relative deviation in the total pressure is 11% for the new correlation whereas it was 8.4% for the former correlation. Similar results are obtained when the experimental results for the pressure required to dissolve ammonia in an aqueous solution of ammonium sulfate by Rumpf and Maurer [1] are compared with the correlations. For the former correlation, the mean relative deviations in the total pressure are 1 and 6% at 433 and 333 K, respectively, whereas those deviations increase to 2.3 and 10% for the new correlation.

Table 6
Readjusted binary and ternary parameters for interactions between ammonia and ammonium sulfate in aqueous solutions at temperatures between 313 and 433 K[a]

	A	B	C	D
$B_{NH_3,(NH_4)_2SO_4}^{(0)}$	0.368567	–	−0.115032	0.0126271
$\Gamma_{NH_3,NH_3,(NH_4)_2SO_4}$	0.457574×10^{-4}	−0.282522	–	–
$\Gamma_{NH_3,(NH_4)_2SO_4,(NH_4)_2SO_4}$	-0.22177×10^{-2}	−1.589616	–	–

[a] $f(T) = A + (B/CT/K) + C(T/100\ \mathrm{K}) + \mathrm{D(T/100\ K)}^2$; $f \equiv (B_{NH_3,NH_4,SO_4}^{(0)}, \Gamma_{NH_3,NH_3,(Na_4)_2SO_4}, \Gamma_{NH_3,NH_4,SO_4,NH_4,SO_4})$.

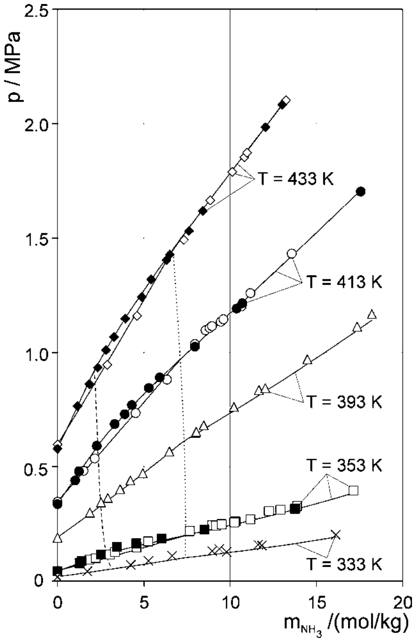

Fig. 3. Solubility of NH_3 in aqueous solutions of Na_2SO_4. Experimental results from [1] and correlation; ×, □, △, ○, ◇: experimental results for $\overline{m}_{Na_2SO_4}=1$ mol/kg H_2O; ■, ●, ◆: experimental results for $\overline{m}_{Na_2SO_4}=2$ mol/kg H_2O; ———: correlation; calculated upper limit of $\overline{m}_{NH_3}$ before Na_2SO_4 precipitates from an aqueous solution (- - -: at $\overline{m}_{Na_2SO_4}=1$ mol/kg H_2O; ···: at $\overline{m}_{Na_2SO_4}=2$ mol/kg H_2O).

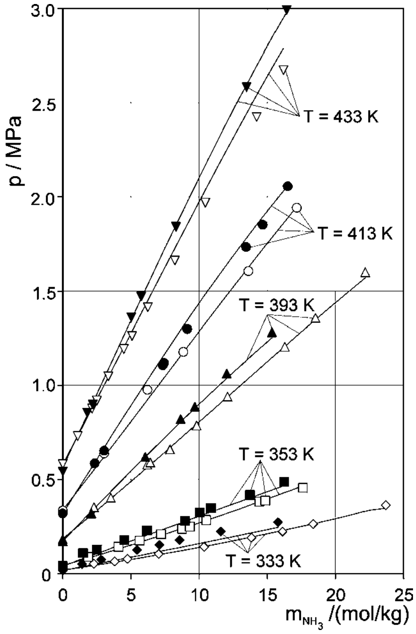

Fig. 4. Solubility of NH_3 in aqueous solutions of $(NH_4)_2SO_4$. Experimental results from [1] and correlation; □, △, ○, ◇, ▽: experimental results for $\overline{m}_{(NH_4)_2SO_4}=2$ mol/kg H_2O; ■, ▲, ●, ◆, ▼: experimental results for $\overline{m}_{(NH_4)_2SO_4}=4$ mol/kg H_2O; —: correlation.

6. Conclusions

New experimental data for the heat of mixing of an aqueous solution of ammonia with an aqueous solution of either sodium sulfate or ammonium sulfate are used together with literature data for the solubility of ammonia in aqueous solutions of one of those salts to describe the influence of temperature on binary and ternary interaction parameters in an extended Pitzer's model for the Gibbs excess energy of aqueous solutions of ammonia, sodium ions, ammonium ions and sulfate ions. Such a model has already been available in the literature, but the parameters for interactions between ammonia and the ions had been determined from gas solubility data alone. Model predictions for the enthalpy of mixing revealed systematic deviation from calorimetric data. The new set of interaction parameters gives a considerably better description of the calorimetric data, for the sake of a somewhat minor agreement with the gas solubility data.

7. Nomenclature

a	activity
A_φ	Debye–Hückel parameter
b	constant
$B^{(0)}_{\mathrm{G,MX}}$	binary parameter for interactions between a gas G and a strong electrolyte MX
C^{Φ}	third osmotic virial coefficient
e	charge of proton
G^{E}	excess Gibbs energy of an aqueous solution (reference states: water: pure liquid; solute: one mol of solute in 1000 g of pure water, but interactions as in infinite dilution; both at (T, p) of the mixture)
$H^{(m)}_{\mathrm{NH_3,w}}$	Henry's constant for the solubility of ammonia in pure water on molality scale
H	enthalpy
I_{m}	ionic strength on molality scale
k	Boltzmann constant

$K_{\mathrm{M,X}}$	solubility product of M_2X
M	molecular mass
M	cation
M_2X	2:1 electrolyte
m	molality
$\tilde{m}$	mass
N_{A}	Avogadro's number
N	number
n	number of moles
$\tilde{n}_i$	total number of moles of component i in mixing cell
p	pressure
Q_{mix}	experimental results for the heat of mixing
R	universal gas constant
T	thermodynamic temperature
$v^{\infty}_{\mathrm{NH_3,w}}$	partial molar volume of ammonia in pure water at infinite dilution
X	anion
y	mole fraction in vapor phase
z_i	number of charges of component i

Greek

α	constant
$\beta^{(0)}, \beta^{(1)}$	binary interaction parameters
δ	uncertainty
Δ	difference
ε_0	vacuum permittivity
ε_{w}	relative dielectric constant of water
$\gamma_i^{(m)}$	activity coefficient of solute i on molality scale
$\gamma^{\pm,(m)}_{\mathrm{M_2X}}$	mean ionic activity coefficient of strong electrolyte M_2X on molality scale
λ	binary interaction parameter
τ	ternary interaction parameter
Γ	ternary interaction parameter
φ	fugacity coefficient
v_+, v_-	stoichiometric coefficients
ρ	density

Subscripts

calc.	calculated
exp.	experimental
i,j,k	components
H_2O	water
liq	liquid
mix	mixing
M	cation
M_2X	2:1 electrolyte
NH_3	ammonia
$NH_3 \leftrightarrow M_2X$	interactions between NH_3 and M_2X
w	water
X	anion

Superscripts

(2)	after mixing
//	vapor phase
lower	in lower compartment before mixing
(m)	on molality scale
upper	in upper compartment before mixing
s	saturation

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Appendix A. Calculation of vapor–liquid equilibrium for the solubility of ammonia in an aqueous solution of a strong (2:1) electrolyte

The vapor–liquid equilibrium is described by extended Raoult's law for water

$$p_{\mathrm{w}}^{\mathrm{s}}(T)\varphi_{\mathrm{w}}^{\mathrm{s}}(T)\exp\left(\frac{p-p_{\mathrm{w}}^{\mathrm{s}}(T)}{\rho_{\mathrm{w,liq}}^{\mathrm{s}}RT}\right)a_{\mathrm{w}} = p y_{\mathrm{w}} \varphi_{\mathrm{w}}^{//} \tag{A.1}$$

and extended Henry's law for ammonia:

$$H^{(m)}_{\mathrm{NH_3,w}}(T)\exp\left(\int_{p_{\mathrm{w}}^{\mathrm{s}}}^{p}\frac{v^{\infty}_{\mathrm{NH_3,w}}(T,p)}{RT}\,\mathrm{d}p\right)m_{\mathrm{NH_3}}\gamma^{(m)}_{\mathrm{NH_3}} = y_{\mathrm{NH_3}} p \varphi^{//}_{\mathrm{NH_3}} \tag{A.2}$$

$H^{(m)}_{\mathrm{NH_3,w}}$ and $v^{\infty}_{\mathrm{NH_3,w}}$ are Henry's constant for the solubility of ammonia in pure water on molality scale and the partial molar volume of ammonia at infinite dilution in water. The fugacity coefficient of pure, saturated water ($\varphi_{\mathrm{w}}^{\mathrm{s}}$), as well as of ammonia ($\varphi^{//}_{\mathrm{NH_3}}$) and water ($\varphi^{//}_{\mathrm{w}}$) were calculated with the virial equation of state truncated after the second coefficient. The activity coefficient of any solute species i (cation, anion and dissolved gas) and the activity of water were calculated from Pitzer's equation for the Gibbs excess energy (cf. from Eq. (2)):

$$\begin{aligned}\ln\gamma_i^{(m)} = {} & -A_\varphi z_i^2\left[\frac{\sqrt{I_\mathrm{m}}}{1+b\sqrt{I_\mathrm{m}}}+\frac{2}{b}\ln\left(1+b\sqrt{I_\mathrm{m}}\right)\right] \\ & +2\sum_{j\neq \mathrm{w}} m_i\Bigg(\beta_{i,j}^{(0)}+\beta_{i,j}^{(1)}\frac{2}{\alpha^2 I_\mathrm{m}} \\ & \times\left(1-\left(1+\alpha\sqrt{I_\mathrm{m}}\right)\exp\left(-\alpha\sqrt{I_\mathrm{m}}\right)\right)\Bigg) \\ & -\frac{z_i^2}{\alpha^2 I_\mathrm{m}^2}\Bigg[1-\left(1+\alpha\sqrt{I_\mathrm{m}}+\frac{\alpha^2}{2}I_\mathrm{m}\right) \\ & \times\exp\left(-\alpha\sqrt{I_\mathrm{m}}\right)\Bigg]\sum_{j\neq \mathrm{w}}\sum_{k\neq \mathrm{w}} m_j m_k \beta_{j,k}^{(1)} \\ & +3\sum_{j\neq \mathrm{w}}\sum_{k\neq \mathrm{w}} m_j m_k \tau_{i,j,k} \qquad \text{(A.3)}\end{aligned}$$

$$\begin{aligned}\ln a_\mathrm{w} = {} & \frac{M_\mathrm{w}}{1000}\Bigg\{2A_\varphi\frac{{I_\mathrm{m}}^{1.5}}{1+b\sqrt{I_\mathrm{m}}}-\sum_{i\neq \mathrm{w}}\sum_{j\neq \mathrm{w}} m_i m_j \\ & \times\left[\beta_{i,j}^{(0)}+\beta_{i,j}^{(1)}\exp\left(-\alpha\sqrt{I_\mathrm{m}}\right)\right] \\ & -2\sum_{i\neq \mathrm{w}}\sum_{j\neq \mathrm{w}}\sum_{k\neq \mathrm{w}} m_i m_j m_k \tau_{i,j,k}-\sum_{i\neq \mathrm{w}} m_i\Bigg\} \qquad \text{(A.4)}\end{aligned}$$

As the solubility of sodium sulfate as well as of ammonium sulfate is reduced when ammonia is dissolved in the aqueous phase, the formation of a solid phase (either Na_2SO_4 or $(NH_4)_2SO_4$) was also taken into account. For a 2:1 electrolyte M_2X the solid–liquid equilibrium is expressed by the solubility product:

$$K_{\mathrm{M_2X}}(T) = \left(m_\mathrm{M}\gamma_\mathrm{M}^{(m)}\right)^2 m_\mathrm{X}\gamma_\mathrm{X}^{(m)} \qquad \text{(A.5)}$$

The precipitation of the salt M_2X is neglected as long as

$$\left(m_\mathrm{M}\gamma_\mathrm{M}^{(m)}\right)^2 m_\mathrm{X}\gamma_\mathrm{X}^{(m)} < K_{\mathrm{M_2X}}(T)$$

The calculations showed that in the range of state of interest in the present work only sodium sulfate, but no ammonium sulfate can precipitate from the aqueous phase. Therefore, only numbers for $K_{\mathrm{Na_2SO_4}}$were required.

All those additional parameters ($H^{(m)}_{\mathrm{NH_3,w}}$, $v^{\infty}_{\mathrm{NH_3,w}}$, $p^{\mathrm{s}}_{\mathrm{w}}$, virial coefficients and $K_{\mathrm{Na_2SO_4}}$) were the same as in a former publication [1].

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