Influence of NH_4Cl, NH_4NO_3, and $NaNO_3$ on the Simultaneous Solubility of Ammonia and Carbon Dioxide in Water

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New experimental results for the simultaneous solubility of ammonia and carbon dioxide in (about 4 *m*) aqueous solutions of NH_4Cl, NH_4NO_3, and $NaNO_3$ at (313, 353, and 393) K and total pressures up to about 0.7 MPa are reported. The maximum loading of carbon dioxide to ammonia, i.e., the molar ratio of carbon dioxide to ammonia, in the liquid phase was about 1 (at 313 K), about 0.7 (at 353 K), and about 0.3 (at 393 K). The experimental results are used to assess predictions from a thermodynamic model for the solubility of ammonia and sour gases in aqueous solutions of strong electrolytes.

Introduction

In the present paper we continue a series of publications on the simultaneous solubility of ammonia and a sour gas in aqueous solutions. Such vapor−liquid equilibria are governed by chemical reactions in the liquid phase as ammonia reacts with the sour gases, resulting in an aqueous, electrolyte solution. The presence of additional components, e.g., strong electrolytes, may have an essential influence on that vapor−liquid equilibrium. Experimental results and thermodynamic models for the simultaneous solubility of ammonia and carbon dioxide in pure water[1−3] as well as in aqueous solutions of sodium sulfate,[4] sodium chloride,[5] and ammonium sulfate and in aqueous solutions of mixtures of ammonium sulfate and sodium sulfate[6] have been presented previously. Furthermore, similar work was performed for aqueous solutions of ammonia and sulfur dioxide,[7] ammonia and phosphoric acid,[8] and ammonia and hydrogen sulfide.[9] Additionally, the solubility of the single gases ammonia,[10,11] carbon dioxide,[12−17] sulfur dioxide,[18−20] and hydrogen sulfide[21−23] in aqueous solutions of strong electrolytes was investigated in recent years. The experimental data were used to determine parameters in a thermodynamic framework to describe the simultaneous solubility of ammonia and a sour gas in aqueous electrolyte solutions.

In this paper we report new experimental data for the influence of three single salts, NH_4Cl, NH_4NO_3, and $NaNO_3$, on the vapor−liquid equilibrium encountered when ammonia and carbon dioxide are simultaneously dissolved in water at 313, 353, and 393 K. In the experiments of the present work the molality of both ammonia and the strong electrolyte was about 4.

When carbon dioxide is added to an aqueous solution of ammonia and a strong electrolyte, the pressure at first drops as in the liquid carbon dioxide neutralizes ammonia and thus converts volatile, neutral ammonia into nonvolatile ionic species: ammonium and carbamate ions. Thus, the partial pressure of ammonia decreases. As carbon dioxide is also converted to nonvolatile species, i.e., bicarbonate, carbamate, and carbonate ions, the decrease of the partial pressure of ammonia cannot be compensated by the very small increase of the partial pressure of carbon dioxide, and as a consequence the total pressure above the aqueous solution also decreases. When more carbon dioxide is added, the conversion rate of the "newly" dissolved carbon dioxide decreases; i.e., carbon dioxide has now to be dissolved in neutral form in the aqueous electrolyte solution. Therefore, both the partial pressure of carbon dioxide and the total pressure increase with further increasing carbon dioxide molality. The molar ratio of "overall" carbon dioxide to "overall" ammonia in such experiments is limited by the upper pressure for which the experimental arrangement is suited. In the present work, that pressure is about 0.7 MPa, resulting in an upper limit for the molar ratio of carbon dioxide to ammonia of about 1 (for each of the salts investigated here at 313 K), about 0.75 and 0.65 (for $NaNO_3$ and (NH_4Cl or NH_4NO_3), respectively, at 353 K), and about 0.45 and 0.25 (for $NaNO_3$ and (NH_4Cl or NH_4NO_3), respectively at 393 K).

When either ammonia or carbon dioxide is dissolved in an aqueous salt-containing solution, the partial pressure of that gas may increase ("salting-out") or decrease ("salting-in"). However, when both gases are simultaneously dissolved in an aqueous salt-containing solution, not only does the presence of the strong electrolyte influence the solubility of each of the gases, but it also has an influence on the chemical reaction equilibria, i.e., on the concentration of the neutral gases. Therefore, and as the partial pressure of water is always decreased by a strong electrolyte, the presence of a strong electrolyte may either increase or decrease the total pressure above such an aqueous solution (for the given temperature and overall liquid-phase molalities of ammonia as well as of carbon dioxide). A thermodynamic framework has been developed in recent work which—by neglecting some interactions in the liquid phase—allows for the prediction of such multicomponent vapor−liquid equilibria from experimental data for the pure component (e.g., the vapor pressure of water), the binary mixtures (e.g., water + salt vapor−liquid equilibrium data and gas solubility data for each of the single gases in water), and the ternary mixtures (the solubility of the single gases in an aqueous solution of the single electrolytes and the simultaneous solubility of ammonia and carbon dioxide in pure water). That model is tested here further by comparing the new experimental data with predictions.

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Experimental Section

The experimental arrangement is basically the same as that used in previous investigations on the simultaneous solubility of ammonia and carbon dioxide in aqueous solutions,[3,5,6,24] and therefore only the principles, but no details, are repeated here.

A high-pressure thermostated cell (volume ~2000 cm^3) is charged with a known amount (about 1 kg) of an about 4 *m* aqueous solution of a single salt. That solution was carefully prepared by dissolving a known amount of the salt into an also known amount of deionized, bidistilled, and degassed water. After the cell has been charged with the aqueous solvent, ammonia is added to achieve an aqueous-phase molality of also about 4. The amount of ammonia is also exactly known as it is taken from a small tank which is weighed before and after the filling procedure. Then in a similar way carbon dioxide is added in several steps. After each step the phases are equilibrated, the temperature, pressure, and vapor-phase volume are measured, and small vapor phase samples are taken and analyzed by gas chromatography. From these direct experimental data the amounts of ammonia and carbon dioxide in the liquid phase are determined. The maximum uncertainty of the experimental results is estimated at ±0.1 K for the temperature, ±0.5 kPa for the total pressure, ±0.1% for the molality of the salt, and ±0.5% for the overall molality of ammonia as well as of carbon dioxide in the liquid phase. The experimental uncertainties for the partial pressures above the liquid phase depend on the experimental conditions. They are given with the detailed experimental results. The following numbers can be regarded as a reasonable estimate: ±2% or ±0.5 kPa (whichever is larger) for the partial pressures of ammonia and carbon dioxide, and (±0.8, ±1.5, and ±5) kPa for the partial pressure of water at (313, 353, and 393) K, respectively.

Substances. Ammonia (>99.999 mol %), carbon dioxide (>99.995 mol %), and the salts (NH_4Cl and $NaNO_3$, >99.4 mass %, NH_4NO_3, >99.0 mass %) were used as supplied. Messer-Griesheim, Ludwigshafen, Germany, supplied both gases, Riedel-de Haen, Seelze, Germany, all salts. Deionized water was degassed by vacuum distillation.

Experimental Results

The simultaneous solubility of carbon dioxide and ammonia ($\bar{m}_{NH_3} \approx 4$ mol/kg) in aqueous solutions of the single salts ammonium chloride ($\bar{m}_{NH_4Cl} \approx 4$ mol/kg), ammonium nitrate ($\bar{m}_{NH_4NO_3} \approx 4$ mol/kg), and sodium nitrate ($\bar{m}_{NaNO_3} \approx 4$ mol/kg) was measured at (313, 353, and 393) K. The pressure ranged up to about 0.7 MPa, corresponding to a maximum molar ratio of carbon dioxide to ammonia in the liquid phase of about 1 at 313 K, about 0.7 at 353 K, and about 0.3 at 393 K. The experimental results for the total pressure and the partial pressures of ammonia, carbon dioxide, and water are given in Tables 1−3, together with estimated uncertainties in the reported variables. Furthermore, the number of phases π_P in the equilibrium cell are given, as for some of the solutions investigated the precipitation of a salt was observed. Experimentally, the precipitation of a salt is ascertained from the time necessary to reach equilibrium (i.e., constant pressure). When no salt precipitates, equilibrium is reached after about 12 h and 3 h at 313 K and 353 K, respectively, whereas if a salt precipitates, about 24 h and 4.5 h are necessary to reach equilibrium at those temperatures. At 393 K, no salt precipitates. The results will be discussed and compared with predictions in one of the following chapters.

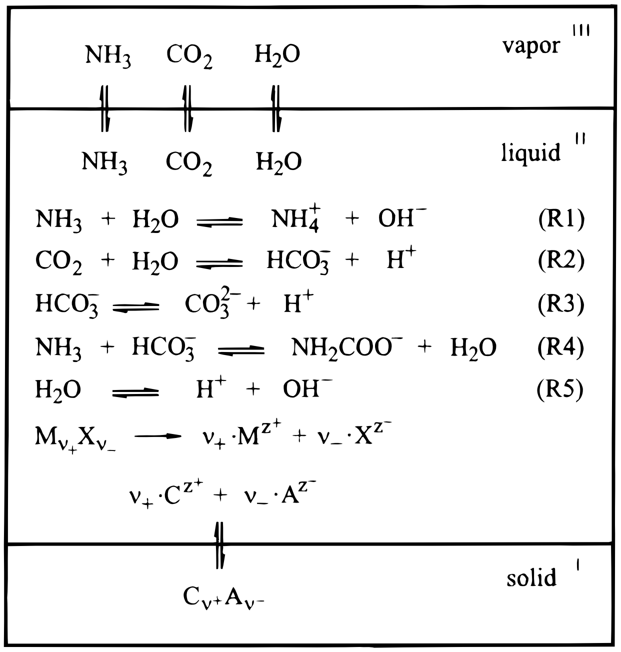

Figure 1. Scheme of the vapor−liquid and vapor−liquid−solid equilibrium of the system $NH_3 + CO_2$ + salt MX + H_2O.

Modeling. Figure 1 shows a scheme of the vapor−liquid equilibrium when ammonia and carbon dioxide are simultaneously dissolved in an aqueous solution of a single salt MX (MX = NH_4Cl, NH_4NO_3, or $NaNO_3$). The vapor−liquid equilibrium is described by the extended Raoult law for water

$$p_W^s(T)\varphi_W^s(T)\exp\left(\int_{p_W^s}^{p}\frac{v_{W,liq}}{RT}\,dp\right)a_W = p y_W \varphi_W''' \qquad (1)$$

and by the extended Henry law for each of the dissolved gases

$$H_{i,W}^{(m)}(T)\exp\left(\int_{p_W^s}^{p}\frac{v_{i,W}^{\infty}}{RT}\,dp\right)m_i\gamma_i^{(m)} = p y_i \varphi_i''' \qquad (2)$$

The molality of gas *i* in the liquid phase differs from the corresponding overall molality as ammonia reacts with carbon dioxide. The model takes into account the following chemical reaction equilibria in the liquid phase: the protonation of ammonia (R1), the formation of bicarbonate (R2), the dissociation of bicarbonate to carbonate (R3), the formation of carbamate from ammonia and bicarbonate (R4), and the autoprotolysis of water (R5). The chemical reaction equilibrium is expressed by

$$K_R(T,p) = \prod_i a_i^{\nu_{i,R}} \qquad R \mathrel{\hat{=}} R1, ..., R5 \qquad (3)$$

where $\nu_{i,R}$ is the stoichiometric factor of component *i* in reaction R ($\nu_{i,R} > 0$ for a product and $\nu_{i,R} < 0$ for an educt). For any dissolved species (but not for the solvent water), the activity a_i is

$$a_i = m_i\gamma_i^{(m)} \qquad (4)$$

However, due to the chemical reactions also bicarbonate ions are present, and as the solubilities of ammonium bicarbonate and sodium bicarbonate in water are rather small, the formation of a solid phase (NH_4HCO_3—when NH_4Cl or NH_4NO_3 is the strong electrolyte—or $NaHCO_3$—

Table 1. Experimental Results for the Simultaneous Solubility of Ammonia and Carbon Dioxide in Aqueous Solutions of Ammonium Chloride in Comparison with Predictions

T/K	$\bar{m}_{NH_4Cl}$/(mol/kg)	$\bar{m}_{NH_3}$/(mol/kg)	$\bar{m}_{CO_2}$/(mol/kg)	p_{NH_3}/bar		p_{CO_2}/bar		p_{H_2O}/bar		p/bar		π_P	
				exptl	pred	exptl	pred	exptl	pred	exptl	pred	exptl	pred
313.16	4.002 ± 0.0027	0	0	0	0	0	0	0.064 ± 0.005	0.064	0.064	0.064	2	2
313.18	4.002 ± 0.0027	3.874 ± 0.004	0	0.133 ± 0.009	0.135	0	0	0.060 ± 0.007	0.060	0.193	0.196	2	2
313.18	4.002 ± 0.0027	3.875 ± 0.004	0.383 ± 0.001	0.113 ± 0.009	0.116	0.000 + 0.003	0.003	0.061 ± 0.007	0.060	0.174	0.178	2	2
313.15	4.002 ± 0.0027	3.878 ± 0.004	0.940 ± 0.001	0.080 ± 0.010	0.085	0.008 ± 0.003	0.011	0.061 ± 0.009	0.060	0.149	0.156	2	2
313.16	4.002 ± 0.0027	3.880 ± 0.004	1.504 ± 0.002	0.046 ± 0.008	0.055	0.039 ± 0.006	0.037	0.062 ± 0.009	0.059	0.147	0.151	2	2
313.15	4.002 ± 0.0027	3.882 ± 0.004	2.071 ± 0.002	0.021 ± 0.007	0.029	0.175 ± 0.013	0.138	0.061 ± 0.008	0.059	0.257	0.227	2	2
313.16	4.002 ± 0.0027	3.883 ± 0.004	2.492 ± 0.003	0.010 ± 0.007	0.017	0.543 ± 0.017	0.364	0.060 ± 0.007	0.059	0.613	0.440	2	2
313.15	4.002 ± 0.0027	3.883 ± 0.004	2.872 ± 0.005	0.006 ± 0.006	0.010	1.316 ± 0.021	0.834	0.058 ± 0.006	0.059	1.380	0.903	2	2
313.16	4.002 ± 0.0027	3.883 ± 0.004	3.237 ± 0.007	0.005 ± 0.005	0.006	2.045 ± 0.026	1.857	0.060 ± 0.007	0.059	2.110	1.922	3	2
313.16	4.002 ± 0.0027	3.884 ± 0.004	3.532 ± 0.010	0.000 + 0.003	0.003	3.472 ± 0.029	3.643	0.059 ± 0.006	0.060	3.531	3.706	3	3
313.16	4.002 ± 0.0027	3.884 ± 0.004	3.737 ± 0.015	0.000 + 0.003	0.002	5.869 ± 0.041	5.971	0.061 ± 0.007	0.062	5.930	6.035	3	3
313.14	4.002 ± 0.0027	3.884 ± 0.004	3.788 ± 0.017	0.000 + 0.003	0.002	6.836 ± 0.045	6.863	0.060 ± 0.006	0.062	6.896	6.928	3	3
353.18	4.001 ± 0.0027	0	0	0	0	0	0	0.415 ± 0.005	0.414	0.415	0.414	2	2
353.17	4.001 ± 0.0027	3.932 ± 0.007	0	0.609 ± 0.019	0.604	0	0	0.376 ± 0.018	0.388	0.985	0.992	2	2
353.16	4.001 ± 0.0027	3.937 ± 0.005	0.314 ± 0.001	0.531 ± 0.019	0.532	0.050 ± 0.004	0.056	0.380 ± 0.018	0.387	0.961	0.976	2	2
353.14	4.001 ± 0.0027	3.942 ± 0.005	0.621 ± 0.001	0.458 ± 0.017	0.462	0.132 ± 0.007	0.139	0.377 ± 0.018	0.387	0.967	0.988	2	2
353.15	4.001 ± 0.0027	3.947 ± 0.004	0.915 ± 0.002	0.375 ± 0.015	0.396	0.264 ± 0.011	0.264	0.386 ± 0.018	0.387	1.025	1.046	2	2
353.18	3.985 ± 0.0027	0	0	0	0	0	0	0.415 ± 0.005	0.415	0.415	0.415	2	2
353.17	3.985 ± 0.0027	1.862 ± 0.004	0	0.284 ± 0.013	0.279	0	0	0.395 ± 0.015	0.402	0.679	0.681	2	2
353.16	3.985 ± 0.0027	3.969 ± 0.007	0	0.612 ± 0.019	0.610	0	0	0.380 ± 0.018	0.388	0.992	0.998	2	2
353.18	3.985 ± 0.0027	3.974 ± 0.005	0.321 ± 0.001	0.536 ± 0.019	0.537	0.049 ± 0.004	0.057	0.382 ± 0.018	0.388	0.967	0.982	2	2
353.15	3.985 ± 0.0027	3.979 ± 0.005	0.624 ± 0.001	0.465 ± 0.017	0.467	0.128 ± 0.007	0.138	0.379 ± 0.018	0.387	0.972	0.992	2	2
353.16	3.985 ± 0.0027	3.984 ± 0.005	0.922 ± 0.002	0.390 ± 0.015	0.400	0.253 ± 0.010	0.261	0.384 ± 0.018	0.387	1.027	1.048	2	2
353.17	3.985 ± 0.0027	3.989 ± 0.004	1.214 ± 0.003	0.323 ± 0.013	0.337	0.464 ± 0.016	0.456	0.380 ± 0.018	0.387	1.167	1.180	2	2
353.15	3.985 ± 0.0027	3.993 ± 0.004	1.493 ± 0.004	0.261 ± 0.011	0.279	0.803 ± 0.022	0.760	0.377 ± 0.019	0.386	1.441	1.425	2	2
353.16	3.985 ± 0.0027	3.997 ± 0.004	1.760 ± 0.005	0.206 ± 0.012	0.228	1.353 ± 0.029	1.230	0.371 ± 0.020	0.387	1.930	1.845	2	2
353.17	3.985 ± 0.0027	4.000 ± 0.004	2.004 ± 0.007	0.162 ± 0.011	0.187	2.162 ± 0.034	1.908	0.381 ± 0.021	0.388	2.705	2.483	2	2
353.16	3.985 ± 0.0027	4.002 ± 0.004	2.198 ± 0.009	0.130 ± 0.010	0.158	3.154 ± 0.038	2.702	0.383 ± 0.022	0.389	3.667	3.249	2	2
353.17	3.985 ± 0.0027	4.003 ± 0.004	2.380 ± 0.011	0.107 ± 0.010	0.135	4.450 ± 0.042	3.733	0.388 ± 0.022	0.390	4.945	4.258	2	2
353.15	3.985 ± 0.0027	4.005 ± 0.004	2.568 ± 0.014	0.086 ± 0.009	0.113	6.393 ± 0.048	5.195	0.390 ± 0.023	0.393	6.869	5.701	2	2
393.16	4.017 ± 0.0027	0	0	0	0	0	0	1.746 ± 0.005	1.737	1.746	1.738	2	2
393.15	4.017 ± 0.0027	3.809 ± 0.011	0	1.717 ± 0.040	1.781	0	0	1.682 ± 0.043	1.641	3.399	3.422	2	2
393.15	4.017 ± 0.0027	3.818 ± 0.010	0.192 ± 0.003	1.594 ± 0.041	1.663	0.482 ± 0.016	0.473	1.651 ± 0.044	1.644	3.727	3.780	2	2
393.14	4.017 ± 0.0027	3.831 ± 0.010	0.381 ± 0.005	1.452 ± 0.041	1.549	1.087 ± 0.031	1.052	1.642 ± 0.046	1.648	4.181	4.249	2	2
393.14	4.017 ± 0.0027	3.843 ± 0.010	0.565 ± 0.008	1.313 ± 0.040	1.441	1.842 ± 0.045	1.752	1.630 ± 0.048	1.652	4.785	4.846	2	2
393.15	4.017 ± 0.0027	3.854 ± 0.009	0.735 ± 0.011	1.190 ± 0.039	1.344	2.727 ± 0.056	2.560	1.613 ± 0.049	1.659	5.530	5.562	2	2
393.15	4.017 ± 0.0027	3.861 ± 0.009	0.860 ± 0.013	1.106 ± 0.037	1.274	3.508 ± 0.064	3.271	1.601 ± 0.050	1.664	6.215	6.208	2	2
393.14	4.017 ± 0.0027	3.866 ± 0.009	0.942 ± 0.015	1.049 ± 0.036	1.228	4.108 ± 0.068	3.800	1.593 ± 0.051	1.667	6.750	6.696	2	2

Table 2. Experimental Results for the Simultaneous Solubility of Ammonia and Carbon Dioxide in Aqueous Solutions of Ammonium Nitrate in Comparison with Predictions

				p_{NH_3}/bar		p_{CO_2}/bar		p_{H_2O}/bar		p/bar		π_P	
T/K	$\bar{m}_{NH_4NO_3}$/(mol/kg)	$\bar{m}_{NH_3}$/(mol/kg)	$\bar{m}_{CO_2}$/(mol/kg)	exptl	pred	exptl	pred	exptl	pred	exptl	pred	exptl	pred
313.17	3.985 ± 0.0022	0	0	0	0	0	0	0.068 ± 0.005	0.067	0.068	0.067	2	2
313.17	3.985 ± 0.0022	2.063 ± 0.003	0	0.065 ± 0.008	0.063	0	0	0.063 ± 0.008	0.065	0.128	0.127	2	2
313.15	3.985 ± 0.0022	4.086 ± 0.006	0	0.132 ± 0.009	0.129	0	0	0.061 ± 0.007	0.063	0.193	0.191	2	2
313.15	3.985 ± 0.0022	4.087 ± 0.004	0.405 ± 0.001	0.116 ± 0.008	0.111	0.000 + 0.003	0.002	0.058 ± 0.007	0.062	0.174	0.175	2	2
313.19	3.985 ± 0.0022	4.090 ± 0.004	0.996 ± 0.001	0.082 ± 0.010	0.083	0.006 ± 0.003	0.007	0.061 ± 0.009	0.062	0.149	0.152	2	2
313.15	3.985 ± 0.0022	4.093 ± 0.004	1.604 ± 0.002	0.047 ± 0.008	0.052	0.033 ± 0.006	0.027	0.062 ± 0.009	0.062	0.142	0.140	2	2
313.15	3.985 ± 0.0022	4.095 ± 0.004	1.998 ± 0.002	0.028 ± 0.007	0.035	0.086 ± 0.010	0.066	0.063 ± 0.009	0.061	0.177	0.163	2	2
313.14	3.985 ± 0.0022	4.096 ± 0.004	2.391 ± 0.003	0.015 ± 0.007	0.022	0.231 ± 0.015	0.165	0.063 ± 0.008	0.061	0.309	0.248	2	2
313.17	3.985 ± 0.0022	4.096 ± 0.004	2.745 ± 0.004	0.009 ± 0.007	0.014	0.548 ± 0.018	0.358	0.063 ± 0.007	0.061	0.620	0.434	2	2
313.16	3.985 ± 0.0022	4.097 ± 0.004	3.101 ± 0.005	0.006 ± 0.006	0.009	1.276 ± 0.022	0.753	0.061 ± 0.007	0.061	1.343	0.822	2	2
313.14	3.985 ± 0.0022	4.097 ± 0.004	3.517 ± 0.008	0.005 ± 0.005	0.004	2.521 ± 0.029	1.834	0.062 ± 0.007	0.062	2.588	1.900	2	2
313.17	3.985 ± 0.0022	4.097 ± 0.004	3.842 ± 0.014	0.002 ± 0.002	0.002	4.720 ± 0.037	4.146	0.062 ± 0.007	0.063	4.784	4.211	2	2
313.16	3.985 ± 0.0022	4.097 ± 0.004	3.985 ± 0.018	0.002 ± 0.002	0.002	6.787 ± 0.054	6.213	0.065 ± 0.007	0.064	6.854	6.279	2	2
353.07	4.014 ± 0.0022	0	0	0	0	0	0	0.431 ± 0.005	0.427	0.431	0.427	2	2
353.12	4.014 ± 0.0022	1.937 ± 0.010	0	0.264 ± 0.012	0.259	0	0	0.406 ± 0.014	0.416	0.670	0.675	2	2
353.18	4.014 ± 0.0022	3.942 ± 0.020	0	0.545 ± 0.018	0.540	0	0	0.391 ± 0.018	0.405	0.936	0.944	2	2
353.18	4.014 ± 0.0022	3.947 ± 0.012	0.326 ± 0.004	0.476 ± 0.018	0.475	0.054 ± 0.004	0.041	0.391 ± 0.018	0.404	0.921	0.921	2	2
353.17	4.014 ± 0.0022	3.953 ± 0.012	0.653 ± 0.004	0.406 ± 0.016	0.410	0.142 ± 0.007	0.107	0.394 ± 0.018	0.404	0.942	0.920	2	2
353.18	4.014 ± 0.0022	3.957 ± 0.011	0.960 ± 0.005	0.343 ± 0.014	0.349	0.278 ± 0.011	0.206	0.394 ± 0.018	0.404	1.015	0.959	2	2
353.17	4.014 ± 0.0022	3.963 ± 0.011	1.281 ± 0.006	0.277 ± 0.012	0.288	0.522 ± 0.017	0.382	0.396 ± 0.019	0.403	1.195	1.073	2	2
353.17	4.014 ± 0.0022	3.966 ± 0.011	1.558 ± 0.007	0.226 ± 0.010	0.238	0.874 ± 0.023	0.638	0.399 ± 0.020	0.403	1.499	1.279	2	2
353.13	4.014 ± 0.0022	3.969 ± 0.011	1.787 ± 0.008	0.189 ± 0.011	0.200	1.298 ± 0.029	0.967	0.399 ± 0.021	0.403	1.886	1.570	2	2
353.15	4.014 ± 0.0022	3.972 ± 0.011	1.992 ± 0.009	0.153 ± 0.011	0.169	1.982 ± 0.034	1.409	0.390 ± 0.022	0.403	2.525	1.982	2	2
353.17	4.014 ± 0.0022	3.974 ± 0.011	2.186 ± 0.011	0.122 ± 0.010	0.144	2.918 ± 0.038	2.004	0.392 ± 0.022	0.404	3.432	2.552	2	2
353.17	4.014 ± 0.0022	3.976 ± 0.011	2.371 ± 0.014	0.103 ± 0.009	0.122	3.876 ± 0.042	2.793	0.394 ± 0.023	0.406	4.373	3.320	2	2
353.17	4.014 ± 0.0022	3.978 ± 0.011	2.626 ± 0.018	0.077 ± 0.009	0.096	6.120 ± 0.050	4.396	0.394 ± 0.023	0.409	6.591	4.900	2	2
393.11	4.009 ± 0.0022	0	0	0	0	0	0	1.763 ± 0.005	1.795	1.763	1.796	2	2
393.12	4.009 ± 0.0022	3.874 ± 0.010	0	1.527 ± 0.038	1.601	0	0	1.721 ± 0.042	1.708	3.248	3.309	2	2
393.13	4.009 ± 0.0022	3.877 ± 0.010	0.113 ± 0.002	1.482 ± 0.039	1.540	0.291 ± 0.010	0.190	1.688 ± 0.042	1.709	3.461	3.440	2	2
393.13	4.009 ± 0.0022	3.883 ± 0.010	0.225 ± 0.004	1.407 ± 0.039	1.482	0.621 ± 0.020	0.405	1.681 ± 0.044	1.711	3.709	3.597	2	2
393.13	4.009 ± 0.0022	3.895 ± 0.009	0.431 ± 0.006	1.277 ± 0.039	1.373	1.356 ± 0.036	0.883	1.669 ± 0.046	1.714	4.302	3.971	2	2
393.13	4.009 ± 0.0022	3.904 ± 0.009	0.610 ± 0.009	1.168 ± 0.038	1.282	2.165 ± 0.049	1.405	1.649 ± 0.048	1.718	4.982	4.405	2	2
393.14	4.009 ± 0.0022	3.914 ± 0.009	0.790 ± 0.012	1.059 ± 0.036	1.191	3.155 ± 0.060	2.063	1.646 ± 0.050	1.724	5.860	4.978	2	2
393.13	4.009 ± 0.0022	3.920 ± 0.009	0.919 ± 0.014	0.986 ± 0.034	1.128	4.024 ± 0.066	2.633	1.634 ± 0.052	1.727	6.645	5.488	2	2

Table 3. Experimental Results for the Simultaneous Solubility of Ammonia and Carbon Dioxide in Aqueous Solutions of Sodium Nitrate in Comparison with Predictions

T/K	$\bar{m}_{NaNO_3}$/(mol/kg)	$\bar{m}_{NH_3}$/(mol/kg)	$\bar{m}_{CO_2}$/(mol/kg)	p_{NH_3}/bar		p_{CO_2}/bar		p_{H_2O}/bar		p/bar		π_P	
				exptl	pred	exptl	pred	exptl	pred	exptl	pred	exptl	pred
313.15	3.988 ± 0.0021	0	0	0	0	0	0	0.067 ± 0.005	0.065	0.067	0.065	2	2
313.15	3.988 ± 0.0021	1.923 ± 0.003	0	0.078 ± 0.009	0.072	0	0	0.060 ± 0.008	0.063	0.138	0.136	2	2
313.16	3.988 ± 0.0021	4.061 ± 0.006	0	0.165 ± 0.009	0.159	0	0	0.057 ± 0.007	0.061	0.222	0.219	2	2
313.16	3.988 ± 0.0021	4.063 ± 0.004	0.408 ± 0.001	0.140 ± 0.009	0.139	0.000 + 0.001	0.000	0.059 ± 0.007	0.061	0.199	0.200	2	2
313.14	3.988 ± 0.0021	4.065 ± 0.004	0.826 ± 0.001	0.112 ± 0.009	0.114	0.000 + 0.001	0.000	0.060 ± 0.008	0.061	0.172	0.175	2	2
313.17	3.988 ± 0.0021	4.069 ± 0.004	1.438 ± 0.001	0.070 ± 0.010	0.071	0.003 ± 0.003	0.003	0.062 ± 0.009	0.061	0.135	0.135	2	2
313.13	3.988 ± 0.0021	4.072 ± 0.004	1.893 ± 0.002	0.041 ± 0.009	0.039	0.019 ± 0.005	0.012	0.062 ± 0.010	0.061	0.122	0.112	2	2
313.14	3.988 ± 0.0021	4.073 ± 0.004	2.101 ± 0.002	0.029 ± 0.008	0.027	0.036 ± 0.007	0.026	0.063 ± 0.010	0.061	0.128	0.114	2	2
313.17	3.988 ± 0.0021	4.073 ± 0.004	2.319 ± 0.002	0.020 ± 0.007	0.019	0.071 ± 0.010	0.057	0.064 ± 0.009	0.061	0.155	0.137	2	2
313.15	3.988 ± 0.0021	4.074 ± 0.004	2.561 ± 0.002	0.017 ± 0.007	0.013	0.089 ± 0.011	0.103	0.065 ± 0.009	0.061	0.171	0.178	3	3
313.16	3.988 ± 0.0021	4.074 ± 0.004	2.821 ± 0.003	0.012 ± 0.007	0.010	0.152 ± 0.014	0.157	0.064 ± 0.008	0.062	0.228	0.229	3	3
313.13	3.988 ± 0.0021	4.074 ± 0.004	3.210 ± 0.003	0.007 ± 0.007	0.006	0.320 ± 0.021	0.322	0.063 ± 0.007	0.062	0.390	0.390	3	3
313.16	3.988 ± 0.0021	4.075 ± 0.004	3.573 ± 0.005	0.005 ± 0.005	0.003	0.851 ± 0.031	0.767	0.062 ± 0.007	0.063	0.918	0.833	3	3
313.15	3.988 ± 0.0021	4.075 ± 0.004	3.886 ± 0.009	0.001 ± 0.001	0.001	2.743 ± 0.040	2.306	0.062 ± 0.007	0.064	2.806	2.371	3	3
313.15	3.988 ± 0.0021	4.075 ± 0.004	3.996 ± 0.014	0.000 + 0.001	0.001	4.715 ± 0.049	3.972	0.063 ± 0.007	0.065	4.778	4.038	3	3
313.14	3.988 ± 0.0021	4.075 ± 0.004	4.064 ± 0.019	0.000 + 0.001	0.001	6.836 ± 0.055	5.724	0.064 ± 0.007	0.066	6.900	5.791	3	3
353.15	3.997 ± 0.0021	0	0	0	0	0	0	0.418 ± 0.005	0.416	0.418	0.416	2	2
353.14	3.997 ± 0.0021	2.004 ± 0.004	0	0.334 ± 0.014	0.315	0	0	0.391 ± 0.015	0.401	0.725	0.717	2	2
353.14	3.997 ± 0.0021	4.067 ± 0.007	0	0.672 ± 0.020	0.654	0	0	0.374 ± 0.018	0.387	1.046	1.041	2	2
353.16	3.997 ± 0.0021	4.075 ± 0.006	0.410 ± 0.001	0.575 ± 0.020	0.565	0.005 ± 0.003	0.001	0.376 ± 0.019	0.389	0.956	0.955	2	2
353.16	3.997 ± 0.0021	4.082 ± 0.005	0.789 ± 0.001	0.483 ± 0.018	0.467	0.028 ± 0.004	0.007	0.373 ± 0.018	0.390	0.884	0.865	2	2
353.15	3.997 ± 0.0021	4.090 ± 0.005	1.184 ± 0.002	0.382 ± 0.016	0.363	0.087 ± 0.006	0.028	0.376 ± 0.017	0.392	0.845	0.782	2	2
353.17	3.997 ± 0.0021	4.098 ± 0.005	1.576 ± 0.002	0.287 ± 0.012	0.262	0.223 ± 0.011	0.086	0.378 ± 0.016	0.393	0.888	0.741	2	2
353.16	3.997 ± 0.0021	4.104 ± 0.004	1.956 ± 0.003	0.204 ± 0.012	0.178	0.524 ± 0.022	0.252	0.378 ± 0.019	0.393	1.106	0.822	2	2
353.17	3.997 ± 0.0021	4.109 ± 0.004	2.303 ± 0.005	0.143 ± 0.010	0.118	1.110 ± 0.032	0.652	0.380 ± 0.020	0.393	1.633	1.164	2	2
353.16	3.997 ± 0.0021	4.112 ± 0.004	2.614 ± 0.008	0.099 ± 0.009	0.081	2.175 ± 0.043	1.457	0.383 ± 0.021	0.393	2.657	1.931	2	2
353.16	3.997 ± 0.0021	4.113 ± 0.004	2.699 ± 0.008	0.087 ± 0.009	0.072	2.618 ± 0.046	1.802	0.381 ± 0.022	0.394	3.086	2.268	2	2
353.16	3.997 ± 0.0021	4.114 ± 0.004	2.789 ± 0.010	0.077 ± 0.009	0.067	3.170 ± 0.050	2.049	0.386 ± 0.022	0.395	3.633	2.511	2	3
353.16	3.997 ± 0.0021	4.114 ± 0.004	2.869 ± 0.011	0.069 ± 0.009	0.063	3.791 ± 0.053	2.295	0.388 ± 0.022	0.396	4.248	2.754	2	3
353.16	3.997 ± 0.0021	4.115 ± 0.004	2.940 ± 0.012	0.062 ± 0.009	0.059	4.446 ± 0.057	2.544	0.389 ± 0.022	0.397	4.897	3.000	2	3
353.16	3.997 ± 0.0021	4.115 ± 0.004	3.018 ± 0.013	0.059 ± 0.009	0.055	4.896 ± 0.061	2.861	0.402 ± 0.023	0.399	5.357	3.315	3	3
353.15	3.997 ± 0.0021	4.116 ± 0.004	3.140 ± 0.016	0.049 ± 0.008	0.049	6.271 ± 0.069	3.466	0.404 ± 0.024	0.401	6.724	3.916	3	3
393.15	4.031 ± 0.0022	0	0	0	0	0	0	1.743 ± 0.005	1.725	1.743	1.725	2	2
393.15	4.031 ± 0.0022	3.891 ± 0.010	0	1.790 ± 0.041	1.812	0	0	1.669 ± 0.043	1.628	3.459	3.440	2	2
393.15	4.031 ± 0.0022	3.919 ± 0.009	0.532 ± 0.002	1.440 ± 0.038	1.439	0.212 ± 0.010	0.022	1.662 ± 0.041	1.649	3.314	3.110	2	2
393.15	4.031 ± 0.0022	3.946 ± 0.008	1.005 ± 0.005	1.123 ± 0.034	1.091	0.948 ± 0.036	0.180	1.640 ± 0.043	1.659	3.711	2.930	2	2
393.15	4.031 ± 0.0022	3.970 ± 0.007	1.432 ± 0.010	0.844 ± 0.029	0.800	2.486 ± 0.066	0.699	1.607 ± 0.047	1.668	4.937	3.168	2	2
393.15	4.031 ± 0.0022	3.982 ± 0.007	1.670 ± 0.014	0.701 ± 0.026	0.657	3.985 ± 0.083	1.373	1.586 ± 0.050	1.674	6.272	3.704	2	2
393.15	4.031 ± 0.0022	3.985 ± 0.007	1.740 ± 0.015	0.665 ± 0.025	0.618	4.526 ± 0.088	1.661	1.583 ± 0.051	1.676	6.774	3.955	2	2

Table 4. Henry's Constants of NH_3 and CO_2 in Pure Water $\ln(H^{(m)}_{i,W}(T,p^s_W)/\mathrm{MPa\cdot kg\cdot mol^{-1}}) = A_i + B_i/(T/K) + C_i \ln(T/K) + D_i(T/K) + E_i/(T/K)^2$

i	A_i	B_i	C_i	D_i	E_i	T/K
NH_3	3.93188	−1879.02	0	0	−355134.1	273−473
CO_2	192.876	−9624.41	−28.7488	0.0144074	0	273−473

Table 5. Partial Molar Volumes at Infinite Dilution in Water

T/K	$v^{\infty}_{NH_3,W}$/(cm^3/mol)	$v^{\infty}_{CO_2,W}$/(cm^3/mol)
313.15	29.57	33.41
353.15	32.14	36.29
393.15	36.15	40.79

when $NaNO_3$ is the strong electrolyte) is also taken into account. For a 1:1 electrolyte CA the solid−liquid equilibrium is expressed by the solubility product:

$$K_{CA}(T,p) = a_C a_A \tag{5}$$

The precipitation of the salt CA is neglected as long as $a_C a_A < K_{CA}(T,p)$.

To determine the true molalities of all species in the liquid phase for the given temperature and overall mole numbers of ammonia ($\bar{n}_{NH_3} = \bar{m}_{NH_3}$), carbon dioxide ($\bar{n}_{CO_2} = \bar{m}_{CO_2}$), water ($\bar{n}_W = 1/M_W$), and salt MX ($\bar{n}_{MX} = \bar{m}_{MX}$) in the condensed phases, the equations for chemical reaction and solid−liquid equilibria have to be solved simultaneously with the mass balance equations

$$\bar{n}_{NH_3} + \bar{n}_{NH_4Cl} + \bar{n}_{NH_4NO_3} = n''_{NH_3} + n''_{NH_4^+} + n''_{NH_2COO^-} + n'_{NH_4HCO_3} \tag{6}$$

$$\bar{n}_{CO_2} = n''_{CO_2} + n''_{HCO_3^-} + n''_{CO_3^{2-}} + n''_{NH_2COO^-} + n'_{NH_4HCO_3} + n'_{NaHCO_3} \tag{7}$$

$$\bar{n}_W = n''_W + n''_{OH^-} + n''_{HCO_3^-} + n''_{CO_3^{2-}} + n'_{NH_4HCO_3} + n'_{NaHCO_3} \tag{8}$$

$$\bar{n}_{NaNO_3} = n''_{Na^+} + n'_{NaHCO_3} \tag{9}$$

$$\bar{n}_{NH_4Cl} = n''_{Cl^-} \tag{10}$$

$$\bar{n}_{NH_4NO_3} + \bar{n}_{NaNO_3} = n''_{NO_3^-} \tag{11}$$

and the condition for electroneutrality of the aqueous phase

$$n''_{NH_4^+} + n''_{H^+} + n''_{Na^+} = n''_{OH^-} + n''_{HCO_3^-} + 2n''_{CO_3^{2-}} + n''_{NH_2COO^-} + n''_{Cl^-} + n''_{NO_3^-} \tag{12}$$

The model requires the following thermodynamic properties: (*i*) Vapor pressure of water, p^s_W. This was taken from Saul and Wagner.[25] (*ii*) Molar volume of liquid water, $v_{W,liq}$, which was approximated by the molar volume of saturated liquid water, $v^s_{W,liq}$, which was also taken from Saul and Wagner.[25] (*iii*) Henry's constants (on the molality scale) for the solubility of NH_3 and CO_2 in pure water. $H^{(m)}_{NH_3,W}$ was taken from Bieling et al.,[4] and $H^{(m)}_{CO_2,W}$ was taken from Rumpf and Maurer[12] (cf. Table 4). (*iv*) Partial molar volumes of NH_3 and CO_2 at infinite dilution in water, $v^{\infty}_{NH_3,W}$ and $v^{\infty}_{CO_2,W}$. Both were taken from Brelvi and O'Connell[26] (cf. Table 5). (*v*) Fugacity coefficients (for saturated water, φ^s_W, and for all components in the vapor phase, φ_i''' (i = water, ammonia, and carbon dioxide)). All fugacity coefficients were calculated from the virial equation of state truncated after the second virial coefficient.

Table 6. Pure Component Second Virial Coefficients

T/K	$B_{W,W}$/(cm^3/mol)	B_{NH_3,NH_3}/(cm^3/mol)	B_{CO_2,CO_2}/(cm^3/mol)
313.15	−930.82	−222.87	−111.97
353.15	−578.14	−163.21	−85.17
393.15	−385.05	−123.34	−64.69

Table 7. Mixed Second Virial Coefficients

T/K	B_{W,NH_3}/(cm^3/mol)	B_{W,CO_2}/(cm^3/mol)	B_{NH_3,CO_2}/(cm^3/mol)
313.15	−285.28	−163.08	−160.76
353.15	−212.47	−128.99	−129.39
393.15	−165.28	−104.27	−105.93

Table 8. Chemical Equilibrium Constants $\ln K_R = A + B/(T/K) + C \ln(T/K) + D(T/K)$

reaction	A	B	C	10^2D	T/K
R1	97.9761	−5930.70	−15.0635	−1.11274	330−475
R2	102.2803	−7742.64	−14.5059	−2.81042	330−475
R3	116.733	−8981.95	−18.1117	−2.22489	330−475
R4	19.8168	552.6886	−4.03995	0.468978	330−475
R5	140.932	−13445.9	−22.4773	0	273−498

Pure component virial coefficients were calculated from correlations given by Rumpf and Maurer,[10,12] which are based on the data collection by Dymond and Smith[27] (cf. Table 6). Mixed virial coefficients were estimated as recommended by Hayden and O'Connell[28] (cf. Table 7). (*vi*) Chemical reaction equilibrium constants (on the molality scale), $K_R(T,p)$ (R ≙ R1, ..., R5). K_{R1} to K_{R4} were taken from Bieling et al.,[4] and K_{R5} was taken from Edwards et al.[29] (cf. Table 8). (*vii*) Solubility products (also on the molality scale) for salts NH_4HCO_3 and $NaHCO_3$, which were taken from Kurz et al.[3] and Brewer,[30] respectively (cf. Table 9). (*viii*) Activity of water, a_W, and activity coefficients, $\gamma_i^{(m)}$, of all solute species, which were calculated from an expression for the Gibbs excess energy G^E.

Gibbs Excess Energy Model. As in previous work, the G^E model of Pitzer[31] is applied here.

$$\frac{G^E}{n_W RTM_W} = f_1(I) + \sum_{i\neq W}\sum_{j\neq W} m_i m_j \lambda_{i,j}(I) + \sum_{i\neq W}\sum_{j\neq W}\sum_{k\neq W} m_i m_j m_k \tau_{i,j,k} \tag{13}$$

$f_1(I)$ is a modified Debye−Hückel contribution

$$f_1(I) = -A_\phi(4I/b)\ln(1 + b\sqrt{I}) \tag{14}$$

where I is the ionic strength

$$I = (1/2)\sum_i z_i^2 m_i \tag{15}$$

b is 1.2 (kg/mol)$^{1/2}$ for all electrolytes. A_ϕ is the Debye−Hückel parameter:

$$A_\phi = \frac{1}{3}(2\pi N_A \rho^s_{W,liq})^{0.5}\left(\frac{e^2}{4\pi\epsilon_0 DkT}\right)^{1.5} \tag{16}$$

The dielectric constant of pure water D was taken from Bradley and Pitzer.[32]

Table 9. Solubility Products ln $K_{CA} = A + B/(T/K) + C(T/K) + D(T/K)^2 + E(T/K)^3 + F(T/K)^4$

precipitate CA	A	B	C	10^3D	10^6E	10^9F	T/K
NH_4HCO_3	8.3413	−2465.319	0	0	0	0	298−333
$NaHCO_3$	41.6572	−2238	−0.346109	1.25678	−1.97620	1.108	298−400

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

$$\lambda_{i,j}(I) = \beta_{i,j}^{(0)} + \beta_{i,j}^{(1)} f_2(x_1) + \beta_{i,j}^{(2)} f_2(x_2) \tag{17}$$

where $x_1 = \alpha_1\sqrt{I}$, $x_2 = \alpha_2\sqrt{I}$, and

$$f_2(x) = (2/x^2)[1 - (1 + x)\exp(-x)] \tag{18}$$

Here $\alpha_1 = 2.0$ and $\alpha_2 = 12.0$.

$\beta_{i,j}^{(0)}$, $\beta_{i,j}^{(1)}$, $\beta_{i,j}^{(2)}$, and $\tau_{i,j,k}$ are binary and ternary interaction parameters which can depend on temperature. As usual, it is assumed that those parameters are symmetric:

$$\beta_{i,j}^{(r)} = \beta_{j,i}^{(r)} \qquad r = 0, 1, 2 \tag{19}$$

$$\tau_{i,j,k} = \tau_{i,k,j} = \tau_{j,i,k} = \tau_{j,k,i} = \tau_{k,i,j} = \tau_{k,j,i} \tag{20}$$

Furthermore, it is common practice to neglect all parameters between ionic species carrying either only positive or only negative charges. “Symmetrical and unsymmetrical mixing terms” (cf. Pitzer[33]) are neglected.

From eq 13 the activity coefficient of a dissolved species i, $\gamma_i^{(m)}$, is

$$\begin{aligned}\ln \gamma_i^{(m)} = {} & -A_\phi {z_i}^2\left[\frac{\sqrt{I}}{1 + \mathrm{b}\sqrt{I}} + \frac{2}{\mathrm{b}}\ln(1 + b\sqrt{I})\right] + \\ & 2\sum_{j\neq W} m_j[\beta_{i,j}^{(0)} - \beta_{i,j}^{(1)} f_2(x_1) + \beta_{i,j}^{(2)} f_2(x_2)] - \\ & {z_i}^2 \sum_{j\neq W}\sum_{k\neq W} m_j m_k[\beta_{j,k}^{(1)} f_3(x_1) + \beta_{j,k}^{(2)} f_3(x_2)] + \\ & 3\sum_{j\neq W}\sum_{k\neq W} m_j m_k \tau_{i,j,k}\end{aligned} \tag{21}$$

where

$$f_3(x) = \frac{1}{Ix^2}\left[1 - \left(1 + x + \frac{x^2}{2}\right)\exp(-x)\right] \tag{22}$$

The activity of water is calculated from eqs 13 and 21 by applying the Gibbs−Duhem equation:

$$\ln a_W = M_W\left\{\frac{G^E}{n_W RT M_W} - \sum_{i\neq W} m_i \ln \gamma_i^{(m)} - \sum_{i\neq W} m_i\right\} \tag{23}$$

For binary systems (water + strong electrolyte $M_{\nu_+}X_{\nu_-}$), it is common practice to report $\beta_{M,X}^{(0)}$, $\beta_{M,X}^{(1)}$, $\beta_{M,X}^{(2)}$, and C_{MX}^{ϕ}. C_{MX}^{ϕ} is the third osmotic virial coefficient, which contains the ternary parameters $\tau_{M,M,X}$ and $\tau_{M,X,X}$:

$$\frac{1}{3}C_{MX}^{\phi} = \left(\frac{\nu_+}{\nu_-}\right)^{1/2}\tau_{M,M,X} + \left(\frac{\nu_-}{\nu_+}\right)^{1/2}\tau_{M,X,X} \tag{24}$$

As there is usually no means to separate the influence of $\tau_{M,M,X}$ from that of $\tau_{M,X,X}$, one of those parameters can be set to zero (here $\tau_{M,X,X} = 0$) and the other parameter is then calculated from (the reported values for) C_{MX}^{ϕ}:

$$(1/3)C_{MX}^{\phi} = \tau_{M,M,X} \qquad \text{1:1 electrolyte} \tag{25}$$

$$(\sqrt{2}/6)C_{MX}^{\phi} = \tau_{M,M,X} \qquad \text{2:1 electrolyte} \tag{26}$$

For binary systems (water + gas G), $\beta_{G,G}^{(0)}$ and $\tau_{G,G,G}$ are usually reported.

For ternary systems (water + strong electrolyte $M_{\nu_+}X_{\nu_-}$ + gas G), i.e., in eq 21 i represents the neutral solute G and j and k stand for a cation M and anion X, the influence of M and X on the solute G cannot be separated, and therefore, it is common practice to use the following comprehensive parameters:

$$B_{G,MX}^{(r)} = \nu_+\beta_{G,M}^{(r)} + \nu_-\beta_{G,X}^{(r)} \qquad r = 0, 1, 2 \tag{27}$$

$$\Gamma_{G,MX,MX} = {\nu_+}^2\tau_{G,M,M} + 2\nu_+\nu_-\tau_{G,M,X} + {\nu_-}^2\tau_{G,X,X} \tag{28}$$

$$\Gamma_{G,G,MX} = \nu_+\tau_{G,G,M} + \nu_-\tau_{G,G,X} \tag{29}$$

$B_{G,MX}^{(1)}$ and $B_{G,MX}^{(2)}$ are rarely needed to describe the solubility of a gas in an aqueous solution of a strong electrolyte. Therefore, they are neglected here. $B_{G,MX}^{(0)}$, $\Gamma_{G,MX,MX}$, and $\Gamma_{G,G,MX}$ are usually reported. In $B_{G,MX}^{(0)}$, one can arbitrarily set either $\beta_{G,M}^{(0)}$ or $\beta_{G,X}^{(0)}$ to zero, in $\Gamma_{G,MX,MX}$, one can arbitrarily set two of the three parameters $\tau_{G,M,M}$, $\tau_{G,M,X}$, and $\tau_{G,X,X}$ to zero, and in $\Gamma_{G,G,MX}$, one can arbitrarily set either $\tau_{G,G,M}$ or $\tau_{G,G,X}$ to zero.

Parameters for the Gibbs Excess Energy Model. The Gibbs excess energy equation requires binary and ternary parameters for interactions between the solute species. Those parameters were adopted from investigations on binary and ternary subsystems.

Parameters for Binary Aqueous Systems.

H_2O + NH_4Cl. The parameters $\beta_{NH_4^+,Cl^-}^{(0)}$, $\beta_{NH_4^+,Cl^-}^{(1)}$, $\beta_{NH_4^+,Cl^-}^{(2)}$, and $\tau_{NH_4^+,NH_4^+,Cl^-}$ were taken from Thiessen and Simonson.[34]

H_2O + NH_4NO_3. The parameters $\beta_{NH_4^+,NO_3^-}^{(0)}$, $\beta_{NH_4^+,NO_3^-}^{(1)}$, and $\tau_{NH_4^+,NH_4^+,NO_3^-}$ reported by Pitzer[35] for 298.15 K were adopted. The influence of temperature on these parameters was neglected.

H_2O + $NaNO_3$. The parameters $\beta_{Na^+,NO_3^-}^{(0)}$, $\beta_{Na^+,NO_3^-}^{(1)}$, and τ_{Na^+,Na^+,NO_3^-} were taken from Sing et al.[11]

H_2O + $NaHCO_3$ and H_2O + Na_2CO_3. The parameters $\beta_{Na^+,HCO_3^-}^{(0)}$, $\beta_{Na^+,HCO_3^-}^{(1)}$, τ_{Na^+,Na^+,HCO_3^-}, $\beta_{Na^+,CO_3^{2-}}^{(0)}$, $\beta_{Na^+,CO_3^{2-}}^{(1)}$, and $\tau_{Na^+,Na^+,CO_3^{2-}}$ were taken from Peiper and Pitzer[36] and Xia et al.[17]

H_2O + NH_3. The parameters $\beta_{NH_3,NH_3}^{(0)}$ and τ_{NH_3,NH_3,NH_3} were taken from Rumpf et al.[37]

All those parameters are given in the Appendix.

Parameters for the Ternary Aqueous System H_2O + NH_3 + CO_2. Kurz et al.[3,5,6] correlated experimental results for the simultaneous solubility of ammonia and carbon dioxide in aqueous solutions. The set of Pitzer parameters given by Kurz et al.[5] is adopted here (cf. the Appendix).

Parameters for Ternary Aqueous Systems. “Gas + Strong Electrolyte + Water”. When Pitzer’s equation is used to describe the solubility of a single gas G in an aqueous solution of a strong electrolyte $M_{\nu_+}X_{\nu_-}$, there are two binary ($\beta_{G,M}^{(0)}$ and $\beta_{G,X}^{(0)}$) and five ternary interaction parameters ($\tau_{G,M,M}$, $\tau_{G,M,X}$, $\tau_{G,X,X}$, $\tau_{G,G,M}$, and $\tau_{G,G,X}$). However, according to eqs 27−29, these seven parameters can be arranged to only three terms: $B_{G,MX}^{(0)}$, $\Gamma_{G,MX,MX}$, and $\Gamma_{G,G,MX}$. So some of the single parameters can be arbitrarily set to zero, while others can be estimated by combining eqs 27−29 for the same gas G and different salts $M_{\nu_+}X_{\nu_-}$. As in previous work, also here the following conventions are applied:

$$\beta^{(0)}_{\mathrm{G,NH_4^+}} = 0 \tag{30}$$

$$\tau_{\mathrm{G,G,NH_4^+}} = 0 \tag{31}$$

$$\tau_{\mathrm{G,M,M}} = \tau_{\mathrm{G,X,X}} = 0 \tag{32}$$

Therefore

$$B^{(0)}_{\mathrm{G,(NH_4)_{\nu_+}X_{\nu_-}}} = \nu_-\beta^{(0)}_{\mathrm{G,X}} \tag{33}$$

$$\Gamma_{\mathrm{G,MX,MX}} = 2\nu_+\nu_-\tau_{\mathrm{G,M,X}} \tag{34}$$

$$\Gamma_{\mathrm{G,G,(NH_4)_{\nu_+}X_{\nu_-}}} = \nu_-\tau_{\mathrm{G,G,X}} \tag{35}$$

In eqs 30−35 G always stands for NH_3 or CO_2.

NH_3 + Strong Electrolyte + Water. $B^{(0)}_{\mathrm{NH_3,(NH_4)_2SO_4}}$, $\Gamma_{\mathrm{NH_3,(NH_4)_2SO_4,(NH_4)_2SO_4}}$, and $\Gamma_{\mathrm{NH_3,NH_3,(NH_4)_2SO_4}}$, as well as $B^{(0)}_{\mathrm{NH_3,Na_2SO_4}}$, $\Gamma_{\mathrm{NH_3,Na_2SO_4,Na_2SO_4}}$, and $\Gamma_{\mathrm{NH_3,NH_3,Na_2SO_4}}$, were adopted from Weyrich et al.[38] They were fitted to the experimental results for the solubility of NH_3 in aqueous solutions of the single electrolytes $(NH_4)_2SO_4$ and $(Na)_2SO_4$ of Rumpf et al.,[10] Bieling et al.,[24] and Kurz et al.[6] and experimental results for the heat of mixing in the same systems.

Combining eqs 27 and 30 gives

$$\beta^{(0)}_{\mathrm{NH_3,Na^+}} = (1/2)(B^{(0)}_{\mathrm{NH_3,Na_2SO_4}} - B^{(0)}_{\mathrm{NH_3,(NH_4)_2SO_4}}) \tag{36}$$

Combining eqs 29 and 31 gives

$$\tau_{\mathrm{NH_3,NH_3,Na^+}} = (1/2)(\Gamma_{\mathrm{NH_3,NH_3,Na_2SO_4}} - \Gamma_{\mathrm{NH_3,NH_3,(NH_4)_2SO_4}}) \tag{37}$$

$\beta^{(0)}_{\mathrm{NH_3,Na^+}}$ and $\tau_{\mathrm{NH_3,NH_3,Na^+}}$ are given in the Appendix (Table 14).

Sing et al.[11] used experimental results for the solubility of ammonia in aqueous solutions of the single strong electrolytes NaCl and $NaNO_3$ to determine $B^{(0)}_{\mathrm{NH_3,MX}}$ and $\Gamma_{\mathrm{NH_3,NH_3,MX}}$ (neglecting $\Gamma_{\mathrm{NH_3,MX,MX}}$). From eqs 27 and 29, the following binary and ternary interaction parameters are derived from these properties:

$$\beta^{(0)}_{\mathrm{NH_3,Cl^-}} = B^{(0)}_{\mathrm{NH_3,NaCl}} - \beta^{(0)}_{\mathrm{NH_3,Na^+}} \tag{38}$$

$$\tau_{\mathrm{NH_3,NH_3,Cl^-}} = \Gamma_{\mathrm{NH_3,NH_3,NaCl}} - \tau_{\mathrm{NH_3,NH_3,Na^+}} \tag{39}$$

$$\beta^{(0)}_{\mathrm{NH_3,NO_3^-}} = B^{(0)}_{\mathrm{NH_3,NaNO_3}} - \beta^{(0)}_{\mathrm{NH_3,Na^+}} \tag{40}$$

$$\tau_{\mathrm{NH_3,NH_3,NO_3^-}} = \Gamma_{\mathrm{NH_3,NH_3,NaNO_3}} - \tau_{\mathrm{NH_3,NH_3,Na^+}} \tag{41}$$

$\beta^{(0)}_{\mathrm{NH_3,Cl^-}}$, $\tau_{\mathrm{NH_3,NH_3,Cl^-}}$, $\beta^{(0)}_{\mathrm{NH_3,NO_3^-}}$, and $\tau_{\mathrm{NH_3,NH_3,NO_3^-}}$ are given in the Appendix (Table 14).

CO_2 + Strong Electrolyte + Water. Rumpf and Maurer[12] determined $B^{(0)}_{\mathrm{CO_2,(NH_4)_2SO_4}}$ and $\Gamma_{\mathrm{CO_2,(NH_4)_2SO_4,(NH_4)_2SO_4}}$, as well as $B^{(0)}_{\mathrm{CO_2,Na_2SO_4}}$ and $\Gamma_{\mathrm{CO_2,Na_2SO_4,Na_2SO_4}}$ (both $\Gamma_{\mathrm{CO_2,CO_2,Na_2SO_4}}$ and $\Gamma_{\mathrm{CO_2,CO_2,(NH_4)_2SO_4}}$ were assumed to be zero) from experimental results for the solubility of CO_2 in aqueous solutions of the single electrolytes $(NH_4)_2SO_4$ and Na_2SO_4. $B^{(0)}_{\mathrm{CO_2,(NH_4)_2SO_4}}$ and $B^{(0)}_{\mathrm{CO_2,Na_2SO_4}}$ were converted to give

$$\beta^{(0)}_{\mathrm{CO_2,Na^+}} = (1/2)(B^{(0)}_{\mathrm{CO_2,Na_2SO_4}} - B^{(0)}_{\mathrm{CO_2,(NH_4)_2SO_4}}) \tag{42}$$

The parameter $\beta^{(0)}_{\mathrm{CO_2,Na^+}}$ is given in the Appendix (Table 14).

Rumpf et al.[13,15] fitted $B^{(0)}_{\mathrm{CO_2,MX}}$ and $\Gamma_{\mathrm{CO_2,MX,MX}}$ to experimental results for the solubility of carbon dioxide in aqueous solutions of the single salts NaCl and $NaNO_3$ (neglecting $\Gamma_{\mathrm{CO_2,CO_2,MX}}$). From eqs 27 and 28, the following binary and ternary interaction parameters are derived:

$$\beta^{(0)}_{\mathrm{CO_2,Cl^-}} = B^{(0)}_{\mathrm{CO_2,NaCl}} - \beta^{(0)}_{\mathrm{CO_2,Na^+}} \tag{43}$$

$$\tau_{\mathrm{CO_2,Na^+,Cl^-}} = (1/2)\Gamma_{\mathrm{CO_2,NaCl,NaCl}} \tag{44}$$

$$\beta^{(0)}_{\mathrm{CO_2,NO_3^-}} = B^{(0)}_{\mathrm{CO_2,NaNO_3}} - \beta^{(0)}_{\mathrm{CO_2,Na^+}} \tag{45}$$

$$\tau_{\mathrm{CO_2,Na^+,NO_3^-}} = (1/2)\Gamma_{\mathrm{CO_2,NaNO_3,NaNO_3}} \tag{46}$$

Furthermore, Rumpf et al.[14] described the experimental results for the solubility of carbon dioxide in aqueous solutions of NH_4Cl with the parameters $B^{(0)}_{\mathrm{CO_2,NH_4Cl}}$ and $\Gamma_{\mathrm{CO_2,NH_4Cl,NH_4Cl}}$ ($B^{(0)}_{\mathrm{CO_2,NH_4Cl}}$ was predicted (cf. eqs 27, 30, and 43), $\Gamma_{\mathrm{CO_2,NH_4Cl,NH_4Cl}}$ was estimated, and $\Gamma_{\mathrm{CO_2,CO_2NH_4Cl}}$ was neglected). Equation 28 gives

$$\tau_{\mathrm{CO_2,NH_4^+,Cl^-}} = (1/2)\Gamma_{\mathrm{CO_2,NH_4Cl,NH_4Cl}} \tag{47}$$

Rumpf et al.[15] described the experimental results for the solubility of carbon dioxide in aqueous solutions of NH_4NO_3 with the parameters $B^{(0)}_{\mathrm{CO_2,NH_4NO_3}}$ and $\Gamma_{\mathrm{CO_2,NH_4NO_3,NH_4NO_3}}$ ($B^{(0)}_{\mathrm{CO_2,NH_4NO_3}}$ was predicted, and $\Gamma_{\mathrm{CO_2,CO_2,NH_4NO_3}}$ was neglected). From eq 28, the following ternary interaction parameter is derived:

$$\tau_{\mathrm{CO_2,NH_4^+,NO_3^-}} = (1/2)\Gamma_{\mathrm{CO_2,NH_4NO_3,NH_4NO_3}} \tag{48}$$

$\beta^{(0)}_{\mathrm{CO_2,Cl^-}}$, $\tau_{\mathrm{CO_2,Na^+,Cl^-}}$, $\beta^{(0)}_{\mathrm{CO_2,NO_3^-}}$, $\tau_{\mathrm{CO_2,Na^+,NO_3^-}}$, $\tau_{\mathrm{CO_2,NH_4^+,Cl^-}}$, and $\tau_{\mathrm{CO_2,NH_4^+,NO_3^-}}$ are given in the Appendix (Table 14).

All Pitzer parameters not mentioned here were set to zero.

Discussion of the New Experimental Data and Comparison with Predictions

In Figures 2−4, the experimental results for the total pressure above aqueous solutions of ammonium chloride, ammonium nitrate, and sodium nitrate, respectively, are plotted versus the overall amount of carbon dioxide—i.e., the amount of carbon dioxide present in the liquid and solid phases—at temperatures of 313, 353, and 393 K. The full lines represent predictions from the model presented before. The dashed lines represent a correlation for the salt-free system ammonia−carbon dioxide−water (Kurz et al.[5]). The dotted line gives the predicted solubility limit for the precipitation of ammonium bicarbonate or sodium bicarbonate. The appearance of those solids was confirmed experimentally by analyzing the solid phases withdrawn from the cell after the completion of each of the series of measurements. Figures 5 and 6 show the partial pressures of ammonia and carbon dioxide above the ammonium nitrate-containing ammoniacal solution at 353 K.

The partial pressure of ammonia decreases with increasing amount of the sour gas in the liquid phase as more and more ammonia is converted into ionic, nonvolatile form (ammonium and carbamate ions). The partial pressure of carbon dioxide at first is very small and increases rapidly

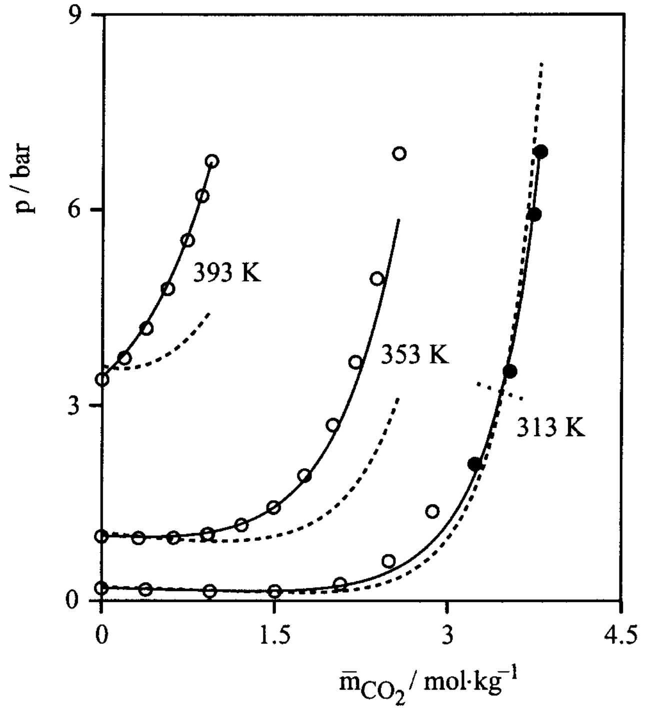

Figure 2. Total pressure in the system $NH_3 + CO_2 + NH_4Cl + H_2O$ ($\bar{m}_{NH_3} \approx 3.9$ mol/kg, $\bar{m}_{NH_4Cl} \approx 4.0$ mol/kg): ○, experimental results VLE, this work; ●, experimental results VLSE, this work; —, prediction, this work; ···, predicted solubility limit of NH_4HCO_3, this work; - - -, calculated results for the system $NH_3 + CO_2 + H_2O$.

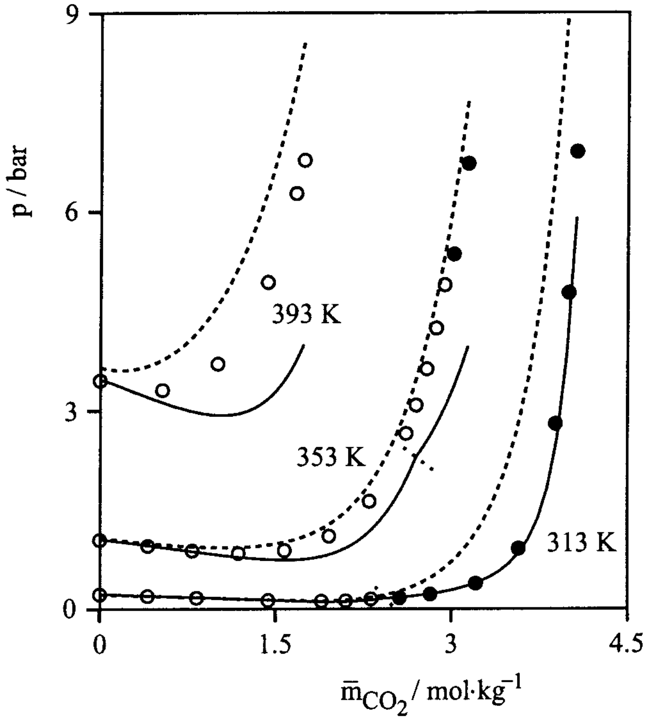

Figure 4. Total pressure in the system $NH_3 + CO_2 + NaNO_3 + H_2O$ ($\bar{m}_{NH_3} \approx 4.0$ mol/kg, $\bar{m}_{NaNO_3} \approx 4.0$ mol/kg): ○, experimental results VLE, this work; ●, experimental results VLSE, this work; —, prediction, this work; ···, predicted solubility limit of $NaHCO_3$, this work; - - -, calculated results for the system $NH_3 + CO_2 + H_2O$.

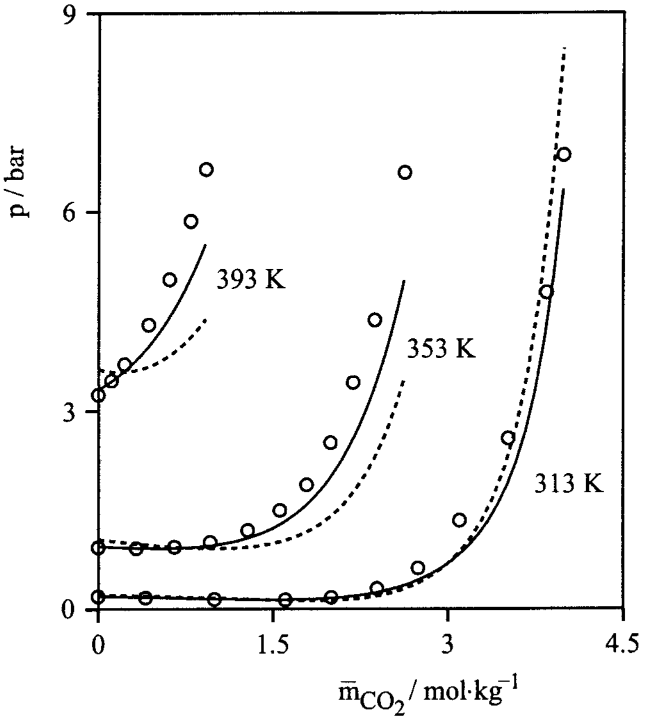

Figure 3. Total pressure in the system $NH_3 + CO_2 + NH_4NO_3 + H_2O$ ($\bar{m}_{NH_3} \approx 4.0$ mol/kg, $\bar{m}_{NH_4NO_3} \approx 4.0$ mol/kg): ○, experimental results VLE, this work; —, prediction, this work; - - -, calculated results for the system $NH_3 + CO_2 + H_2O$.

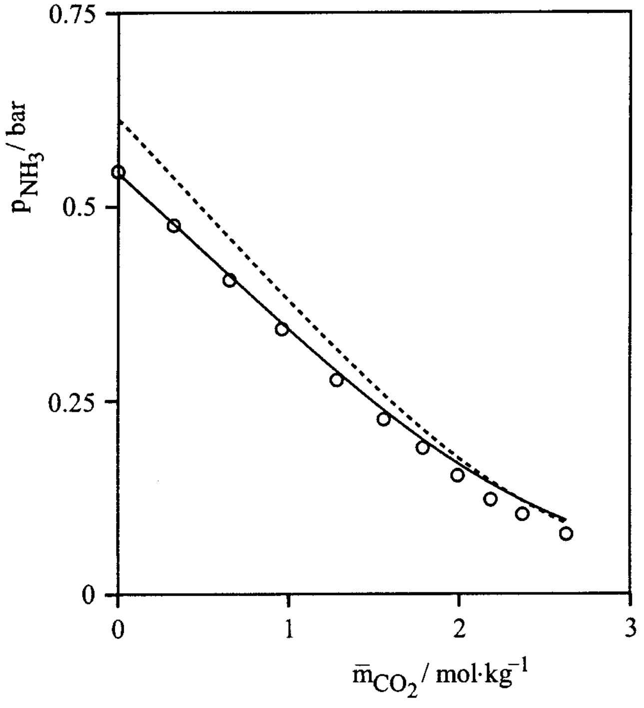

Figure 5. Partial pressure of NH_3 in the system $NH_3 + CO_2 + NH_4NO_3 + H_2O$ at 353 K ($\bar{m}_{NH_3} \approx 4.0$ mol/kg, $\bar{m}_{NH_4NO_3} \approx 4.0$ mol/kg): ○, experimental results VLE, this work; —, prediction, this work; - - -, calculated results for the system $NH_3 + CO_2 + H_2O$.

when in the liquid-phase ammonia has been spent by chemical reactions.

The behavior of the quaternary systems is very similar to that observed for the salt-free system. But the salt causes significant effects, which are discussed here—as an example—for the system $NH_3 + CO_2 + NH_4NO_3 + H_2O$. As can be seen from Figure 5, ammonia is *salted in* by ammonium nitrate; i.e., the partial pressure of ammonia above the salt-containing solution is below that above the salt-free solution. The effect decreases with increasing

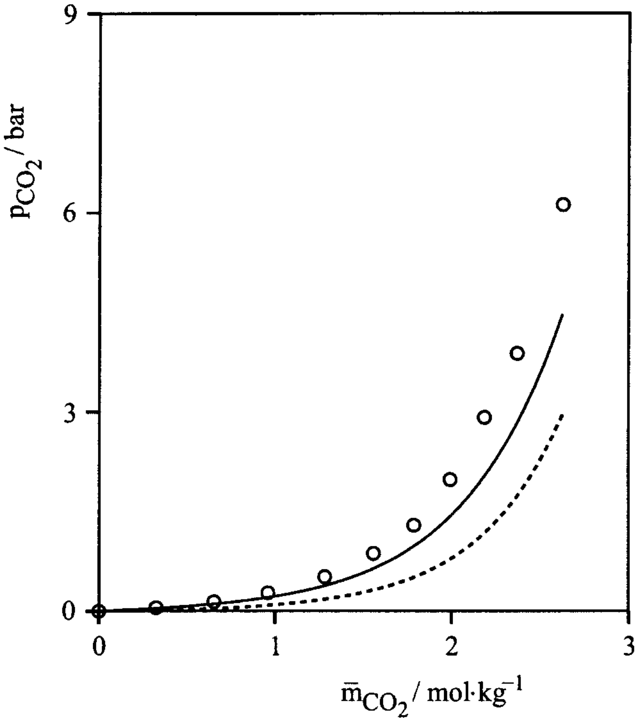

Figure 6. Partial pressure of CO_2 in the system $NH_3 + CO_2 + NH_4NO_3 + H_2O$ at 353 K ($\bar{m}_{NH_3} \approx 4.0$ mol/kg, $\bar{m}_{NH_4NO_3} \approx 4.0$ mol/kg): ○, experimental results VLE, this work; —, prediction, this work; - - -, calculated results for the system $NH_3 + CO_2 + H_2O$.

Table 10. Summarized Comparison between Experimental and Predicted Results

			av rel dev/%[a]				av abs dev/bar			
MX	*T*/K	N	p	p_{NH_3}	p_{CO_2}	p_W	p	p_{NH_3}	p_{CO_2}	p_W
NH_4Cl	313	10	10.0	31.4	16.3	2.3	0.12	0.004	0.12	0.001
	353	13	5.3	9.8	9.4	1.7	0.21	0.015	0.22	0.006
	393	6	0.97	11.0	5.1	2.3	0.046	0.13	0.14	0.036
NH_4NO_3	313	10	14.7	22.9	23.7	2.2	0.26	0.003	0.26	0.001
	353	10	14.6	8.9	27.0	2.5	0.49	0.012	0.51	0.010
	393	6	9.2	8.9	34.8	3.4	0.51	0.10	0.67	0.056
$NaNO_3$	313	13	7.2	12.1	16.0	2.7	0.19	0.002	0.19	0.002
	353	13	24.6	9.1	49.2	2.9	0.91	0.014	0.91	0.011
	393	5	29.1	4.3	74.3	3.4	1.63	0.034	1.64	0.055

[a] Data points with $p \leq 50$ kPa and $p_i \leq 50$ kPa omitted.

amount of the sour gas present in the liquid phase. However, as shown in Figure 6, carbon dioxide is *salted out*; i.e., the partial pressure of carbon dioxide above the salt-containing solution is larger than that above the salt-free solution. Without ammonia, carbon dioxide is salted in by ammonium nitrate (cf. Rumpf et al.[15]). The change from salting in to salting out in the presence of ammonia is due to the strong influence of ammonium nitrate on the chemical reactions in the liquid phase. The partial pressure of water is reduced by ammonium nitrate, but it is only slightly changed when both gases are dissolved. For the total pressure (cf. Figure 3), salting in is observed at low carbon dioxide concentrations—mainly due to the reduction of the partial pressure of ammonia—whereas at higher molalities the competition of salting out of carbon dioxide and salting in of ammonia results in a higher pressure than that above the salt-free solution. At 313 K the total pressure above the ammonium nitrate-containing solution is higher than above the salt-free solution only at intermediate carbon dioxide molalities.

The experimental results for the total pressure and partial pressures of ammonia, carbon dioxide, and water above $NH_3 + CO_2 +$ salt $MX + H_2O$, with $MX = NH_4Cl$, NH_4NO_3, and $NaNO_3$, as well as the number of phases π_P in the equilibrium cell, are compared with predictions in Tables 1−3. Additionally, a summarized comparison is given in Table 10

For $MX = NH_4Cl$ (cf. Figure 2), the model gives a good representation of the experimental data. At 313 K, and for carbon dioxide molalities up to about 2 mol/kg and above 3 mol/kg, the predictions agree within experimental uncertainties with the experimental data for the total and partial pressures. At this temperature, the model predicts the precipitation of NH_4HCO_3 at a carbon dioxide concentration of about 3.46 mol/kg. But experimentally, this salt already precipitates at a lower carbon dioxide molality (between 2.87 and 3.24 mol/kg). At 353 K and 393 K, the agreement between experimental and predicted results is very satisfactory. At 353 K, larger deviations are observed at high molalities of carbon dioxide, where the increase in the total pressure curve is rather steep.

For $MX = NH_4NO_3$ (cf. Figures 3, 5, and 6) the model is only able to qualitatively predict the experimental results. The best agreement is achieved at 313 K. The discrepancies at higher temperatures may result from poor numbers for the interaction parameters for the binary subsystem ammonium nitrate−water. Reliable numbers for those parameters are only available for 298 K,[39] and due to the lack of experimental data, these numbers had to be adopted also for higher temperatures.

For $MX = NaNO_3$ (cf. Figure 4) most predictions agree only qualitatively with the experimental results. A quantitative agreement is achieved only at 313 K. The discrepancies at higher temperatures might again result from poor numbers for the interaction parameters for the binary subsystem sodium nitrate-water. Reliable parameters are only available for 298 K.[39] The influence of temperature on these parameters was estimated by Sing et al.[11] using some experimental data for the total pressure above aqueous solutions of sodium nitrate. At 313 K and 353 K, the model predicts the precipitation of $NaHCO_3$ at a carbon dioxide concentration of about 2.44 and 2.70 mol/kg, respectively. Experimentally, this salt precipitates at carbon dioxide molalities between 2.32 and 2.56 mol/kg at 313 K and between 2.94 and 3.02 mol/kg at 353 K.

For some experimental data points, particularly at high molalities of carbon dioxide, the prediction results in rather large deviations in the total pressure and the partial pressure of carbon dioxide. These deviations occur when the increase in the total pressure curve is rather steep, and the total pressure is dominated by the amount of neutraly dissolved carbon dioxide. As that amount is small in comparison to the overall amount of dissolved carbon dioxide, i.e., in either ionic or neutral form, very small absolute deviations in the amount of neutral carbon dioxide result in large deviations in the total pressure. Figure 7 illustrates the influence of a salt (here $NaNO_3$) on the species distribution, and consequently on the total and partial pressures. Predictions are shown for "true" molalities of all solute species (except H^+ and OH^-) present in the liquid phase for a solution with $\bar{m}_{NH_3} = 4$ mol/kg (dashed lines) at 353 K (without a salt), when carbon dioxide is added. As expected, adding carbon dioxide to an ammoniacal solution reduces the neutral amount of ammonia, thereby producing ammonium, carbamate, bicarbonate, and carbonate ions. Figure 7 also shows predicted true molalities of all solute species present in the liquid phase for a salt-containing solution with $\bar{m}_{NH_3} = \bar{m}_{NaNO_3} = 4$ mol/kg (full lines) at the same temperature, when carbon

Table 11. Coefficients of Eqs A1 and A2

	$\beta^{(0)}_{\mathrm{NH_4^+,Cl^-}}$	$\beta^{(1)}_{\mathrm{NH_4^+,Cl^-}}$	$\beta^{(2)}_{\mathrm{NH_4^+,Cl^-}}$	$3\tau_{\mathrm{NH_4^+,Cl^-}}$
q_1	-9.29689×10^{-1}	6.73399×10^{-1}	-1.7141×10^{2}	-2.79772×10^{-3}
q_2	2.20237×10^{-1}	-1.42555×10^{-1}	-0.19554	
q_3	-1.03306×10^{-3}	1.09395×10^{-3}	-7.4581×10^{-5}	-7.41476×10^{-6}
q_4	5.49192×10^{-7}		4.534	
q_5	-9.15057×10^{-1}		3.505×10^{-2}	9.09242×10^{-2}
q_6				2.12227×10^{-1}
q_7	4.88766×10^{-2}			
q_8	-1.09552×10^{-2}			
q_9	5.61713×10^{-5}			
q_{10}	-3.62817×10^{-8}			
q_{11}	1.93572×10^{-2}			

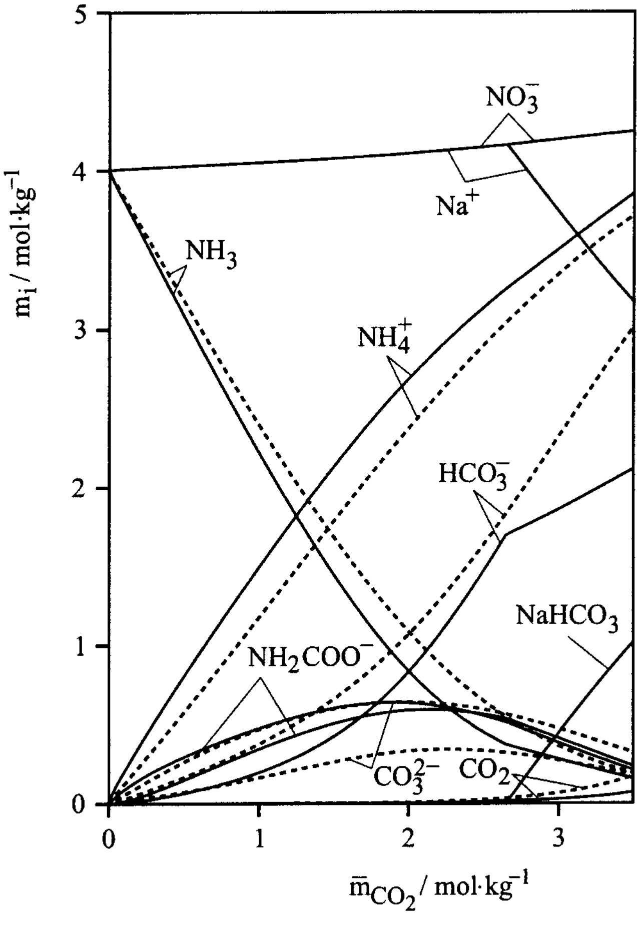

Figure 7. Predicted species distribution in the $NH_3 + CO_2 + NaNO_3 + H_2O$ system at 353 K ($\bar{m}_{NH_3} = 4.0$ mol/kg, $\bar{m}_{NH_4NO_3} = 4.0$ mol/kg).

Table 12. Coefficients of Eq A9

	q_1	$10^3 q_2$	$10^5 q_3$
$\beta^{(0)}_{\mathrm{Na^+,HCO_3^-}}$	0.00389	0.058	0.151
$\beta^{(1)}_{\mathrm{Na^+,HCO_3^-}}$	0.0401	0.298	1.94
$3\tau_{\mathrm{Na^+,Na^+,HCO_3^-}}$	0.00168		
$\beta^{(0)}_{\mathrm{Na^+,CO_3^{2-}}}$	0.0362	1.79	−2.11
$\beta^{(1)}_{\mathrm{Na^+,CO_3^{2-}}}$	1.51	2.05	−8.4
$(6/\sqrt{2})\tau_{\mathrm{Na^+,Na^+,CO_3^{2-}}}$	0.0052		

dioxide is added. Furthermore, the number of moles of solid $NaHCO_3$ per kilogram of water is shown. When the solubility limit of $NaHCO_3$ is surpassed, the increase in the concentration of HCO_3^- is damped. One recognizes the large shift in the species concentration due to the presence of the salt. Of particular interest is the influence of the salt on the concentration of carbon dioxide: For example, for a solution containing an overall amount of carbon dioxide of 3 mol/kg, the predicted amount of neutral carbon dioxide is 0.065 mol/kg, when no sodium nitrate is present (i.e., 97.8% of carbon dioxide is dissolved in ionic form), and 0.027 mol/kg, when this salt is present (i.e., 99.1% of carbon dioxide is dissolved in ionic form or as solid $NaHCO_3$). The total pressure and partial pressure of carbon dioxide above the salt-free solution are 6.66 MPa and 6.14 MPa, respectively, whereas above the salt-containing solution, predicted pressures come to 3.58 MPa and 3.13 MPa, respectively. Thus, in the salt-free system 2.2% of the overall molality of carbon dioxide causes 92.2% of the total pressure, whereas in the salt-containing system 0.9% of the overall molality of carbon dioxide causes 87.4% of the total pressure. This example demonstrates that even very small uncertainties in predictions of the composition of the liquid (and solid) phases lead to a large uncertainty in the predictions of the concentration of neutraly dissolved carbon dioxide and consequently also for the pressures.

Conclusions

The solubility of carbon dioxide in aqueous solutions of ammonia (4 *m*) and a salt—ammonium chloride, ammonium nitrate, or sodium nitrate (also 4 *m*)—was measured in the temperature range from 313 K to 393 K at total pressures up to 0.7 MPa. The results are compared with predictions. The model applied for these predictions is based on investigations of binary and ternary subsystems. The model is able to quantitatively predict the effects caused by ammonium chloride nearly over the complete temperature and composition ranges considered in the present work. Reliable numbers for the interaction parameters for the binary subsystems ammonium nitrate—water and sodium nitrate—water are only available at temperatures around 298 K. Therefore, only at 313 K the model quantitatively predicts the effects resulting from these salts, whereas at higher temperatures the model gives only a qualitative agreement. The calculated results for the pressure in the system containing one of the nitrates can be improved by fitting some additional interaction parameters. Such a procedure might be reasonable for some applications, but from a more general point of view, is not recommended as long as there is still a lack of reliable experimental data for the vapor—liquid equilibrium of the binary systems $H_2O + NH_4NO_3$ and $H_2O + NaNO_3$ at elevated temperatures.

List of Symbols

A	anion A
A_i...E_i	coefficients for the temperature dependence of the Henry's constant for the solubility of gas *i* in pure water
A...*F*	coefficients for the temperature dependence of the solubility product of precipitate *i*

$A...D$	coefficients for the temperature dependence of the chemical equilibrium constant of reaction R
a_i	activity of component i
A_ϕ	Debye−Hückel parameter
b	constant in the modified Debye−Hückel expression
$B_{i,j}$	second virial coefficient for interactions between components i and j
$B_{\mathrm{G,MX}}^{(\mathrm{r})}$	effective second osmotic virial coefficient in Pitzer's equation for interactions between gas G and salt MX ($r = 0, 1, 2$)
C	cation C
C^ϕ	third osmotic virial coefficient in Pitzer's equation
D	relative dielectric constant of water
e	charge of a proton
f	function for the temperature dependence of an interaction parameter
f_1, f_2, f_3	functions in Pitzer's equation
G	gas (here NH_3 and CO_2)
G^{E}	excess Gibbs energy
$H_{i,\mathrm{W}}^{(\mathrm{m})}$	Henry's constant for the solubility of gas i in pure water (on the molality scale)
I	ionic strength (on the molality scale)
k	Boltzmann constant
K_{R}	equilibrium constant for chemical reaction R (on the molality scale)
K_{CA}	solubility product for precipitate CA (on the molality scale)
m_i	true molality of component i
$\bar{m}_i$	overall molality of component i
M	cation M
M_{W}	molar mass of water (kg/mol)
n_i	true number of moles of component i
$\bar{n}_i$	overall number of moles of component i
N	number of data points
N_{A}	Avogadro's number
p	pressure
p_i	partial pressure of component i
$q_1...q_{11}$	coefficients for the temperature dependence of interaction parameters
R	universal gas constant
T	absolute temperature
v	partial molar volume
x, x_1, x_2	variables in Pitzer's equations
X	anion X
y	vapor-phase mole fraction
z_i	number of charges of component i

Greek Letters

α_1, α_2	constants in Pitzer's equation
$\beta^{(0)}, \beta^{(1)}, \beta^{(2)}$	binary interaction parameters in Pitzer's equation
$\gamma_i^{(\mathrm{m})}$	activity coefficient of component i normalized to infinite dilution (on the molality scale)
Γ	third osmotic virial coefficient in Pitzer's equation
ϵ_0	vacuum permittivity
λ	second virial coefficient in Pitzer's equation
$\nu_{i,\mathrm{R}}$	stoichiometric factor of component i in reaction R
ν_+, ν_-	number of cations and anions in electrolytes MX and CA
π_{P}	number of phases
ρ	mass density
τ	third virial coefficient in Pitzer's equation
φ	fugacity coefficient

Subscripts

G	gas
i, j, k	component i, j, k
liq	liquid
MX	strong electrolyte
R	reaction
W	water

Superscripts

(m)	on the molality scale
s	saturation
∞	infinite dilution in pure water
$'$	solid phase
$''$	liquid phase
$'''$	vapor phase

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Appendix

Parameters of the Gibbs Excess Energy Model. In the following equations for binary and ternary Pitzer interaction parameters, T is the temperature (K) ($T_{\mathrm{R}} = 298.15$ K) and p is the pressure (MPa). p is approximated here by the saturation pressure of water $p_{\mathrm{W}}^{\mathrm{s}}$.

H_2O + NH_4Cl. The parameters $\beta^{(0)}_{\mathrm{NH_4^+,Cl^-}}$, $\beta^{(1)}_{\mathrm{NH_4^+,Cl^-}}$, $\beta^{(2)}_{\mathrm{NH_4^+,Cl^-}}$, and $\tau_{\mathrm{NH_4^+,NH_4^+,Cl^-}}$ were taken from Thiessen and Simonson.[34] The influence of temperature on $\beta^{(0)}_{\mathrm{NH_4^+,Cl^-}}$, $\beta^{(1)}_{\mathrm{NH_4^+,Cl^-}}$, and $\tau_{\mathrm{NH_4^+,NH_4^+,Cl^-}}$ (for temperatures from 298 to 523 K) is given by

$$f(T) = q_1 + q_2 \ln T + q_3 T + q_4 T^2 + \frac{q_5}{T - 227} + \frac{q_6}{647 - T} + (p - 7)\left[q_7 + q_8 \ln T + q_9 T + q_{10} T^2 + \frac{q_{11}}{647 - T}\right] \quad \text{(A1)}$$

For $\beta^{(2)}_{\mathrm{NH_4^+,Cl^-}}$ that influence is given by

$$\beta^{(2)}_{\mathrm{NH_4^+,Cl^-}}(T) = q_1\left[q_2 + q_3 T + \frac{q_4}{T} + q_5 \ln T + \frac{1}{647 - T}\right] \quad \text{(A2)}$$

The coefficients of eqs A1 and A2 are given in Table 11.

H_2O + NH_4NO_3. Kim and Frederick[39] gave the parameters $\beta^{(0)}_{\mathrm{NH_4^+,NO_3^-}}$, $\beta^{(1)}_{\mathrm{NH_4^+,NO_3^-}}$, and $\tau_{\mathrm{NH_4^+,NH_4^+,NO_3^-}}$ for 298.15 K. These parameters were adopted; i.e., the influence of temperature on those parameters was neglected.

$$\beta^{(0)}_{\mathrm{NH_4^+,NO_3^-}} = -0.01476 \quad \text{(A3)}$$

$$\beta^{(1)}_{\mathrm{NH_4^+,NO_3^-}} = 0.13826 \quad \text{(A4)}$$

$$3\tau_{\mathrm{NH_4^+,NH_4^+,NO_3^-}} = 0.00029 \quad \text{(A5)}$$

Table 13. Pitzer Parameters for $NH_3 + CO_2 + H_2O$ $f(T) = q_1 + q_2/T$

	q_1	q_2		q_1	q_2
$\beta^{(0)}_{NH_3,HCO_3^-}$	0.2857	−99.466	$\beta^{(0)}_{NH_4^+,CO_3^{2-}}$	−0.146044	
$\beta^{(0)}_{NH_3,CO_3^{2-}}$	−0.3391	151.28	$\tau_{CO_2,NH_4^+,HCO_3^-}$	−0.00112637	
$\beta^{(0)}_{NH_3,NH_2COO^-}$	−0.03933	25.263	$\tau_{NH_4^+,NH_4^+,HCO_3^-}$	0.000507152	
$\beta^{(0)}_{CO_2,HCO_3^-}$	0.0843007	−16.148	$\tau_{NH_4^+,NH_4^+,CO_3^{2-}}$	0.01400683	
$\beta^{(0)}_{NH_4^+,HCO_3^-}$	0.113346	−45.679			

Table 14. Coefficients of Eq A12

	q_1	q_2	10^3q_3	10^6q_4	$10^{-3}q_5$	$10^{-6}q_6$	T/K
$\beta^{(0)}_{NH_3,Na^+}$	0.14716		−0.54102	0.53314			313−433
τ_{NH_3,NH_3,Na^+}	4.1567×10^{-4}	−0.18982					
$\beta^{(0)}_{NH_3,Cl^-}$	−0.12282	−0.17183	0.54102	−0.53314			313−393
τ_{NH_3,NH_3,Cl^-}	-7.2857×10^{-4}	0.18982					
$\beta^{(0)}_{NH_3,NO_3^-}$	−0.14431	2.71305	0.54102	−0.53314			313−393
τ_{NH_3,NH_3,NO_3^-}	-8.13568×10^{-4}	0.18982					
$\beta^{(0)}_{CO_2,Na^+}$	−0.166568	110.662			−11.3475		313−433
$\beta^{(0)}_{CO_2,Cl^-}$	0.4206	−187.486			0.69128	6.31239	313−433
τ_{CO_2,Na^+,Cl^-}	-14.194×10^{-4}						
$\beta^{(0)}_{CO_2,NO_3^-}$	0.69697	−487.256			82.9977		313−433
τ_{CO_2,Na^+,NO_3^-}	-109.632×10^{-4}	7.85296			−1.44314		
τ_{CO_2,NH_4^+,Cl^-}	−0.00175						313−433
$\tau_{CO_2,NH_4^+,NO_3^-}$	-153.342×10^{-4}	10.6726			−1.83602		313−433

***$H_2O + NaNO_3$*.** The parameters $\beta^{(0)}_{Na^+,NO_3^-}$, $\beta^{(1)}_{Na^+,NO_3^-}$, and τ_{Na^+,Na^+,NO_3^-} were taken from Sing et al.[11] for temperatures from 274 to 473 K.

$$\beta^{(0)}_{Na^+,NO_3^-} = 0.00388 + 0.04938(1 - T_R/T) \qquad (A6)$$

$$\beta^{(1)}_{Na^+,NO_3^-} = 0.21151 + 8.6493(1 - T_R/T) \qquad (A7)$$

$$\tau_{Na^+,Na^+,NO_3^-} = -0.00002 - 0.0001(1 - T_R/T) \qquad (A8)$$

Note that there is a typographical error in the equation for τ_{Na^+,Na^+,NO_3^-} given by Sing et al.[11]

***$H_2O + NaHCO_3$ and $H_2O + Na_2CO_3$*.** Interaction parameters for $H_2O + NaHCO_3$ were derived from data given by Peiper and Pitzer[36] and from experimental results for the solubility of $NaHCO_3$ in water at temperatures between 270 K and 373 K (cf. Xia et al.[17]). Peiper and Pitzer[36] reported a correlation for the interaction parameters for $H_2O + Na_2CO_3$ derived from experimental data at temperatures between 273 K and 323 K. This correlation was adopted also for temperatures up to 393 K.

$$f(T) = q_1 + q_2(T - T_R) + q_3(T - T_R)^2 \qquad (A9)$$

Parameters and coefficients of eq A9 are given in Table 12.

***$H_2O + NH_3$*.** Rumpf et al.[37] correlated literature data for the solubility of ammonia in water between 293 K and 413 K and for the enthalpy change accompanying the dilution of an aqueous solution of ammonia with Pitzer's equation. These results were adopted here:

$$\beta^{(0)}_{NH_3,NH_3} = -0.01979 + 9.864/T \qquad (A10)$$

$$\tau_{NH_3,NH_3,NH_3} = 5.539 \times 10^{-3} - 0.1789/T - 8.61 \times 10^{-4} \ln T \qquad (A11)$$

***$H_2O + NH_3 + CO_2$*.** Kurz et al.[3,5,6] described experimental results for the simultaneous solubility of ammonia and carbon dioxide in water and in aqueous solutions of some strong electrolytes applying Pitzer's expression for the excess Gibbs energy of the aqueous solution. The set of parameters given, e.g., by Kurz et al.[5] is based on the assumption that both $\beta^{(0)}_{NH_3,NH_4^+}$ and $\beta^{(0)}_{CO_2,NH_4^+}$ are zero. Nine binary and ternary parameters were additionally necessary to give a reliable description of the experimental data for the vapor−liquid equilibrium of $H_2O + NH_3 + CO_2$ at temperatures between about 313 K and 473 K. Those parameters are given in Table 13.

***H_2O + Gas (G) + Strong Electrolyte (MX)*.** The influence of cation M or anion X on the dissolved neutral solute G is considered by binary and ternary interaction parameters $\beta^{(0)}_{G,M}$, $\beta^{(0)}_{G,X}$, $\tau_{G,M,X}$, $\tau_{G,G,X}$, and $\tau_{G,G,M}$. The influence of the temperature on these parameters is described by

$$f(T) = q_1 + \frac{q_2}{T} + q_3T + q_4T^2 + \frac{q_5}{T^2} + \frac{q_6}{T^3} \qquad (A12)$$

Parameters and coefficients of eq A12 are given in Table 14.

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