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Solubility of CO_2 in Aqueous Solutions of KCl and in Aqueous Solutions of K_2CO_3

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A high-pressure view-cell technique based on the synthetic method was used to determine the total pressure above aqueous solutions of two single salts (potassium chloride and potassium carbonate) and carbon dioxide. In the series of measurements with potassium chloride, the molality of the salt amounted to about (2 and 4) mol·(kg of water)$^{-1}$, the temperature ranged from about (313 to 433) K, and the molality of carbon dioxide ranged up to about 1 mol·(kg of water)$^{-1}$, corresponding to a maximum pressure of about 9.4 MPa. In the series of measurements with potassium carbonate, the stoichiometric molality of that salt amounted to about (0.43 and 1.7) mol·(kg of water)$^{-1}$ (stoichiometric mass fraction of the salt of about 0.056 and 0.19, respectively), the temperature ranged from about (313 to 393) K, and the ratio of the stoichiometric molalities of carbon dioxide to potassium carbonate ranged from about 0.7 to 3.6, corresponding to pressures from about (0.27 to 9.2) MPa. The vapor−liquid equilibrium of the systems (CO_2 + KCl + H_2O) and (CO_2 + K_2CO_3 + H_2O) (the latter allowing for the precipitation of $KHCO_3$ that is important in connection with the “Hot Potassium Carbonate (Benfield) Process” and its modifications by activating additives) is described by means of a thermodynamic model based on Pitzer’s molality scale based equation for the Gibbs excess energy of the aqueous phase. Model parameters are determined from the new carbon dioxide solubility data as well as from an extensive database adopted from the literature.

Introduction

The so-called “Hot Potassium Carbonate (Benfield) Process” uses aqueous potassium carbonate solutions for removal of sour gases carbon dioxide and hydrogen sulfide from ammonia synthesis gas, natural gas, crude hydrogen, etc. by “chemical” absorption.[1−4] The gas absorption takes place at temperatures well above ambient (around 343 K and higher) and at elevated pressures (up to about 2 MPa or more), whereas gas desorption (that is, solvent regeneration in the stripper) occurs at elevated temperatures (up to about 403 K) and low pressures (in particular at low partial pressures of the sour gases). The absorption of carbon dioxide in aqueous solutions of potassium carbonate is hampered by slow chemical reaction kinetics. In particular, the formation of bicarbonate is kinetically hindered.[5] However, relatively high temperature in the absorber highly enhances the absorption rate of carbon dioxide. In addition, high temperature greatly increases the solubility of potassium bicarbonate, therefore allowing operation with highly concentrated solutions.[6] Typically, the stoichiometric mass fraction of potassium carbonate in water ranges from about 0.2 to 0.3 {stoichiometric potassium carbonate molalities from about (1.8 to 3.1) mol·(kg of water)$^{-1}$},[6] but it may reach up to 0.4 {4.8 mol·(kg of water)$^{-1}$}.[3] Process modifications intend to further accelerate the absorption of carbon dioxide by activating additives. Furthermore, to impede corrosion, appropriate inhibitors are added. For example, the so-called “Catacarb Process” uses aqueous solutions of potassium carbonate and an undisclosed additive that incorporates a corrosion-inhibiting component.[6] In most cases, the absorption of carbon dioxide is promoted by the addition of secondary and primary amines,[7,8] for example, diethanolamine (DEA), which is the original Benfield activator,[6] piperazine,[9,10] or even ammonia. These substances quickly and reversibly chemically react with carbon dioxide to form not only carbamate species but also bicarbonate through so-called “reversion” of the carbamate species.

Deviation from equilibrium provides the driving force in a kinetically controlled process. Therefore, to properly design and optimize the separation equipment, equilibrium properties (mainly the chemical reaction equilibrium, the vapor−liquid equilibrium (VLE) as well as information on the energy to vaporize/condense the mixtures) need to be known. In particular, modeling the phase equilibrium for the simultaneous solubility of carbon dioxide and hydrogen sulfide in aqueous solutions of potassium carbonate plus additives requires a reliable and extensive experimental database on the solubility of the single gases in aqueous solutions of potassium carbonate as well as in aqueous solutions of the single additives. The present work focuses on one of the interesting subsystems, namely, (CO_2 + K_2CO_3 + H_2O). A thermodynamic model for describing the VLE of the system (CO_2 + K_2CO_3 + H_2O), which also accounts for the precipitation of potassium bicarbonate ($KHCO_3$), is developed. The model is based on Pitzer’s molality scale-based equation for the Gibbs excess energy of the aqueous phase. Model parameters describing interactions between potassium and carbonate ions are based on experimental data for the vapor pressure above aqueous solutions of potassium carbonate as compiled from the literature by Aseyev.[11] These parameters are valid for temperatures from about 298 K up to at least 473 K and for stoichiometric mass fractions of potassium carbonate in water up to at least 0.5 {stoichiometric molalities of 7.2 mol·(kg of water)$^{-1}$}. Model parameters mainly describing interactions between potassium and bicarbonate ions but also between potassium, bicarbonate, and carbonate ions in the *low* gas loading (low pressure) region (that is, at stoichiometric molar ratios of carbon dioxide to potassium carbonate below one) are

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determined from an extensive equilibrium database. That database covers experimental results by Tosh et al.[3] for the solubility of carbon dioxide in aqueous solutions of potassium carbonate [at temperatures from about 343 K up to 413 K, stoichiometric mass fractions of potassium carbonate from 0.2 to 0.4 {stoichiometric molalities from about (1.8 to 4.8) mol·(kg of water)$^{-1}$}, stoichiometric molar ratios of carbon dioxide to potassium carbonate from 0.1 to about 0.88, and partial pressures of carbon dioxide up to about 0.92 MPa]. In addition, the database includes experimental data for the solubility of the salt potassium bicarbonate in water and in aqueous solutions of carbon dioxide and potassium carbonate (for temperatures from 273 K to 415 K).[1,12,13]

Furthermore, in the present work a high-pressure view-cell technique based on the synthetic method is used to determine the solubility pressure of carbon dioxide above aqueous solutions of potassium chloride. The molality of the salt amounts to about (2 and 4) mol·(kg of water)$^{-1}$, the temperature ranges from about (313 to 433) K, and the molality of carbon dioxide ranges up to about 1 mol·(kg of water)$^{-1}$, corresponding to a maximum pressure of about 9.4 MPa. These new carbon dioxide solubility data in aqueous solutions of potassium chloride are used to determine model parameters describing interactions between carbon dioxide and potassium ions in aqueous solutions. Those parameters are thereby valid for temperatures from (313 to 433) K, so they cover the relevant temperature range for the Hot Potassium Carbonate Process. By including these parameters in the model for the VLE of the system ($CO_2 + K_2CO_3 + H_2O$), the model allows us to make predictions of the carbon dioxide solubility pressure in the *high* gas loading region, where it is difficult to gain experimental information. To evaluate the model predictions, a few new experimental results for the solubility of carbon dioxide in aqueous solutions of potassium carbonate were taken in the high gas loading region—again by means of the high-pressure view-cell technique mentioned above. In these experimental series, the stoichiometric molality of potassium carbonate amounted to about (0.43 and 1.7) mol·(kg of water)$^{-1}$ (stoichiometric mass fraction of the salt of about 0.056 and 0.19, respectively), the temperature ranged from about (313 to 393) K, and the ratio of the stoichiometric molalities of carbon dioxide to potassium carbonate ranged from about 0.7 to 3.6, corresponding to pressures from about (0.27 to 9.2) MPa. The model is able to reliably predict these new experimental results in the high gas loading region. Finally, the few experimental data for the solubility of carbon dioxide in aqueous solutions of either potassium chloride or potassium carbonate found in the open literature are compared with predicted results from the new model.

Experimental Section

Apparatus and Method. The apparatus used to measure the solubility of carbon dioxide in the given solvent (an aqueous solution of either potassium chloride or potassium carbonate) is based on the synthetic method. The equipment is particularly suited for elevated pressures from about 0.2 MPa up to 20 MPa and more. Its central part is an equilibrium cell with a known volume (approximately 30 cm^3). Prior to the series of gas solubility measurements, the cell volume is accurately determined at a fixed temperature by means of a high-precision displacement pump (Ruska Instrument Corporation, Houston, TX, type 2241). Proper corrections are applied to account for the small amount of thermal expansion. At any temperature, the volume of the cell is known to within ± 0.1 %. Details on the gas solubility measuring technique can be found in previous publications.[14−17]

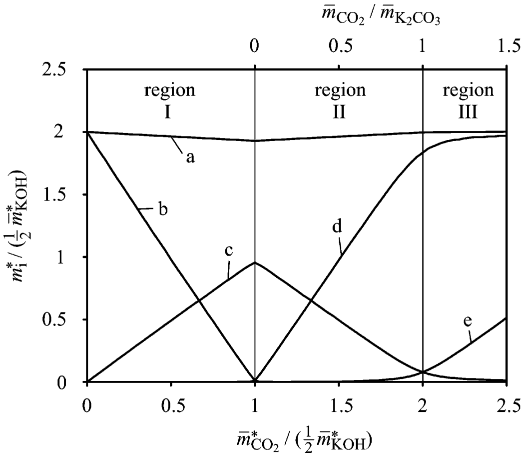

Figure 1. Estimated speciation (a, K^+; b, OH^-; c, CO_3^{2-}; d, HCO_3^-; e, CO_2) in aqueous solutions of (CO_2 + KOH) at $T = 353.15$ K, $\bar{m}_{KOH}^* = 4$ mol·kg^{-1}. (Comments on this figure are given in the text and in Appendix 1.)

In an experiment, the pressure which is required to dissolve, at a constant and preset temperature, a precisely known amount of gas in a precisely known amount of solvent is determined. When the mass of carbon dioxide, which is filled into the cell is small {here smaller than about 1.3 g, which was the case for all CO_2 solubility measurements in (KCl + H_2O)}, it is determined volumetrically from the known volume of the cell and readings for temperature and pressure by applying an appropriate equation of state.[18] When the mass of the gas filled into the cell is large {here larger than about 1.3 g and up to about 6 g, which was the case for all CO_2 solubility measurements in ($K_2CO_3 + H_2O$)}, it is determined gravimetrically by weighing a condenser from which the cell is charged, before and after the charging process on a high-precision balance. Gravimetric uncertainties amount to ± 0.012 g. The mass of solvent filled into the cell (approximately 30 g) is calculated from the volume displacement in a calibrated spindle press and the solvent density with a relative uncertainty of about 0.15 %. The density of the solvent is known from separate measurements with a vibrating-tube densimeter (Anton Paar GmbH, Graz, Austria).

Two calibrated platinum resistance thermometers were used to determine the temperature. The uncertainty of the temperature measurement is better than ± 0.1 K. When carbon dioxide was volumetrically filled into the cell, the pressure was measured with two pressure transducers suitable for pressures ranging up to (2.5 and 4) MPa, respectively. The solubility pressure itself was measured with two other pressure transducers suitable for pressures up to (6 and 10) MPa, respectively. Commercially available electronic pressure transducers (WIKA GmbH, Klingenberg, Germany) were used. The maximum systematic uncertainty in the solubility pressure measurement results from the uncertainty of the pressure transducers (0.1 % of the transducer's full scale) and an additional contribution of about ± 0.01 MPa caused by a small temperature drift in the isolated tubes filled with solvent, which connect the cell with the pressure transducers. The temperature drift contribution was determined in test runs. All pressure transducers were calibrated against a high-precision pressure gauge (Desgranges & Huot, Aubervilliers, France) before and after each series of measurements.

Preliminary Comments. Figure 1 shows a predicted speciation in an aqueous solution of potassium hydroxide and carbon dioxide, where $\bar{m}_{KOH}^*$ and $\bar{m}_{CO_2}^*$ denote the "stoichiometric" molality of these two components {that is, the amount of substance (the number of moles) of a component per kilogram of water} and where m_i^* denotes the "true" molality of all solute species i {that is, the "true" amount of substance (the "true" number of moles) of solute species i per "true" kilogram of water} present in appreciable amounts, namely, potassium (K^+), hydroxide (OH^-), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), and molecular carbon dioxide (CO_2). The speciation was calculated by adopting the chemical reaction equilibrium constants (for the hydrolysis of water and for the formation of carbonate and bicarbonate) from the literature[19−21] and by estimating the activity coefficients of all species from Pitzer's modification of the Debye−Hückel term alone.[22,23]

There are three regions. In region I ($\bar{m}^*_{CO_2}/\bar{m}^*_{KOH} < 1/2$), carbon dioxide almost completely reacts with potassium hydroxide to form potassium carbonate and water:

$$CO_2(aq) + 2KOH(aq) \rightarrow K_2CO_3(aq) + H_2O(l) \qquad (I)$$

In this region, the liquid mixture can be regarded as an aqueous solution of potassium carbonate and potassium hydroxide, where carbon dioxide has been practically completely chemically absorbed. Hence, in region I, the partial pressure of carbon dioxide above the solution is almost zero.

In regions II and III ($1/2 < \bar{m}^*_{CO_2}/\bar{m}^*_{KOH} < 1$ and $\bar{m}^*_{CO_2}/\bar{m}^*_{KOH} > 1$, respectively), the liquid mixture can be regarded as an aqueous solution of potassium carbonate, potassium bicarbonate, and carbon dioxide:

$$CO_2(aq) + K_2CO_3(aq) + H_2O(l) \rightleftharpoons 2KHCO_3(aq) \qquad (II)$$

In region II, most carbon dioxide is chemically absorbed, but some carbon dioxide is dissolved physically, which results in a small but appreciable partial pressure of the gas above the solution. In region III, a considerable amount of carbon dioxide is physically dissolved, which results in a remarkable increase of the total pressure with an increase in the amount of the dissolved gas. Consequently, in connection with the design of absorption/desorption processes of carbon dioxide in such potassium containing solutions, only regions II and III are of importance. In this context, it is therefore reasonable to express the composition of such solutions by the stoichiometric molalities of carbon dioxide (the absorbed acid gas) and potassium carbonate (as the basic electrolyte) ($\bar{m}_{CO_2}$, $\bar{m}_{K_2CO_3}$). Region II ($0 < \bar{m}_{CO_2}/\bar{m}_{K_2CO_3} < 1$) may be denominated as the low gas loading (low pressure) region, and region III ($\bar{m}_{CO_2}/\bar{m}_{K_2CO_3} > 1$) may be denominated as the high gas loading (high pressure) region. The equations to convert the stoichiometric molalities ($\bar{m}^*_{KOH}$ and $\bar{m}^*_{CO_2}$) to ($\bar{m}_{K_2CO_3}$ and $\bar{m}_{CO_2}$) are given in Appendix 1.

Materials and Sample Pretreatment. Deionized water was degassed by vacuum distillation. Carbon dioxide (mole fraction ≥ 99.995 %) was purchased from Messer-Griesheim (Ludwigshafen, Germany). It was used without further purification. Potassium chloride (p.a., mass fraction ≥ 99.5 %) and potassium hydroxide hydrate (p.a., mass fraction KOH ≥ 85 %, mass fraction K_2CO_3 < 1 %, rest is mainly water) were purchased from Merck GmbH (Darmstadt, Germany). They were degassed and dried under vacuum for several hours.

The aqueous solutions of the strong electrolytes (either KCl or KOH) were prepared in a storage tank. The gravimetric uncertainty of the stoichiometric molality of KCl was smaller than about ± 0.02 %. The stoichiometric molality of KOH was determined titrimetrically with a relative uncertainty smaller than about ± 1.6 %. The resulting relative uncertainty of the stoichiometric molality of K_2CO_3 in the aqueous solution is smaller than ± 1.6 %. For the CO_2 solubility measurements in ($KCl + H_2O$), where the gas was volumetrically filled into the cell, the experimental uncertainty of the gas molality is estimated not to surmount 1 %. For the CO_2 solubility measurements in ($KOH + H_2O$), where the gas was gravimetrically filled into the cell, the estimated experimental uncertainty in the gas molality, resulting only from the gas filling procedure, ranges from about 0.25 % (at the highest gas solubilities) to a maximum of 0.9 % (at the lowest gas solubilities). In ($CO_2 + K_2CO_3 + H_2O$), the experimental uncertainty of the gas molality ranges from 0.4 % (at the highest gas solubilities) to a maximum of 2 % (at the lowest gas solubilities).

Experimental Results. (a) System ($CO_2 + KCl + H_2O$). The solubility of carbon dioxide in aqueous solutions of potassium chloride was investigated at salt molalities $\bar{m}_{KCl} \approx$ (2 and 4)

Table 1. Experimental Results for the Total Pressure above Aqueous Solutions of Potassium Chloride and Carbon Dioxide

T	$\bar{m}_{KCl}$	$\bar{m}_{CO_2}$	p	T	$\bar{m}_{KCl}$	$\bar{m}_{CO_2}$	p
K	mol·kg^{-1}	mol·kg^{-1}	MPa	K	mol·kg^{-1}	mol·kg^{-1}	MPa
315.8	1.994	0.1235	0.7354	313.2	4.05	0.0896	0.5878
313.25		0.1390	0.7694	313.1		0.2082	1.414
316.15		0.2941	1.823	313.15		0.2115	1.427
313.25		0.3052	1.833	313.1		0.2241	1.503
313.25		0.4340	2.641	313.15		0.2245	1.536
313.35		0.6210	4.003	313.2		0.3651	2.554
313.6		0.8213	5.854	313.2		0.3666	2.617
313.6		1.0197	8.567	313.1		0.5130	3.775
333.1	1.994	0.2831	2.390	313.1		0.6718	5.437
333.15		0.2837	2.417	313.15		0.7838	6.940
333.15		0.4201	3.715	313.1		0.8739	8.738
333.15		0.5491	5.088	313.3		0.8867	9.320
333.15		0.6709	6.679	313.2		0.8862	9.395
333.15		0.8215	9.016	333.1	4.05	0.2118	2.044
353.0	1.942	0.0374	0.4084	333.15		0.3456	3.482
353.05		0.1771	1.851	333.1		0.4644	4.927
353.0		0.1765	1.861	333.1		0.5557	6.292
353.05		0.3111	3.352	333.1		0.6228	7.337
353.05		0.4295	4.860	333.15		0.7225	9.137
353.05		0.5637	6.784	353.1	4.05	0.1614	2.035
353.05		0.6787	8.714	353.1		0.2983	3.896
373.05	1.942	0.0427	0.6019	353.1		0.3975	5.405
373.05		0.1456	1.850	353.1		0.4795	6.833
373.05		0.1468	1.880	353.15		0.5878	8.909
373.1		0.2612	3.385	373.05	3.998	0.0384	0.6092
373.1		0.3749	4.995	373.05		0.1150	1.720
373.1		0.5398	7.701	373.05		0.1747	2.633
373.1		0.5795	8.591	373.05		0.2879	4.508
393.1	1.942	0.0641	1.046	373.05		0.4005	6.653
393.1		0.1421	2.129	373.05		0.4056	6.755
393.1		0.1431	2.159	373.05		0.4706	8.156
393.1		0.2885	4.331	373.05		0.5070	9.031
393.1		0.3995	6.205	393.05	3.998	0.0378	0.7669
393.1		0.4746	7.612	393.05		0.1104	1.964
393.05		0.5487	9.064	393.05		0.1105	1.974
413.05	1.942	0	0.3361	393.05		0.1852	3.295
413.05		0.0368	0.8632	393.1		0.3029	5.538
413.1		0.1182	2.080	393.05		0.3767	7.079
413.1		0.1183	2.081	393.05		0.4573	9.065
413.1		0.1872	3.168	413.1	3.998	0	0.3078
413.1		0.3122	5.230	413.0		0.0372	0.9535
413.05		0.3809	6.511	413.0		0.1189	2.453
413.05		0.4690	8.170	413.05		0.1953	3.930
433.05	1.942	0	0.5725	413.0		0.1958	3.932
433.05		0.0334	1.072	413.1		0.2719	5.520
433.05		0.1643	3.137	413.05		0.3325	6.856
433.1		0.3033	5.488	413.05		0.4073	8.662
				433.05	3.998	0	0.5248
				433.0		0.0526	1.509
				433.05		0.0538	1.529
				433.0		0.1206	2.835
				433.05		0.1866	4.209
				433.05		0.2627	5.846
				433.05		0.3412	7.653
				433.05		0.3787	8.597

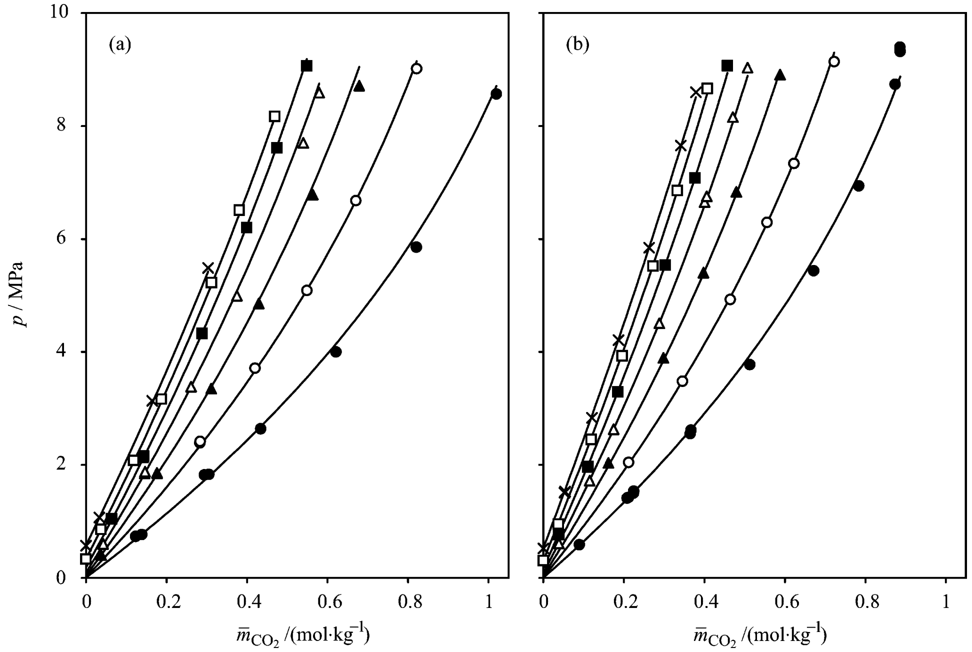

Figure 2. Total pressure above aqueous solutions of (KCl + CO_2) (a, $\bar{m}_{KCl} \approx 2$ mol·kg^{-1}; b, $\bar{m}_{KCl} \approx 4$ mol·kg^{-1}): ●, $T \approx 313.5$ K; ○, $T \approx 333.1$ K; ▲, $T \approx 353.1$ K, △, $T \approx 373.1$ K; ■, $T \approx 393.1$ K; □, $T \approx 413.1$ K; ×, $T \approx 433$ K) experimental results; —, correlation results.

mol·(kg of water)$^{-1}$ at temperatures T from about (313 to 433) K in about 20 K intervals and at pressures p up to about 9.4 MPa. The experimental results are given in Table 1. Figure 2 shows them plotted as the pressure against the gas molality $\bar{m}_{CO_2}$ at a preset temperature.

As can be seen from Figure 2 and according to Henry's law, initially the solubility pressure increases practically linearly with increasing gas molality at a given temperature. Furthermore, at a preset pressure and salt molality, the solubility of CO_2 in (KCl + H_2O) decreases with rising temperature. For example, at $p = 6$ MPa, $\bar{m}_{KCl} \approx 2$ mol·kg^{-1}, and $T \approx$ (313, 353, and 413) K, the solubility of carbon dioxide amounts to $\bar{m}_{CO_2} \approx$ (0.83, 0.5, and 0.36) mol·kg^{-1}, respectively. Figure 3 illustrates the "salting-out" effect induced by the presence of potassium chloride in the aqueous solution, meaning that at a preset temperature and pressure, the gas solubility is reduced by the presence of the salt. For example, at $T \approx 313.15$ K, $p = 6$ MPa, and $\bar{m}_{KCl} \approx$ (0, 2, and 4) mol·kg^{-1}, the solubility of carbon dioxide amounts to $\bar{m}_{CO_2} \approx$ (1, 0.83, and 0.7) mol·kg^{-1}, respectively. The broken curve in Figure 3 gives the correlation results for the solubility of carbon dioxide in pure water (at $T = 313.15$ K) according to Rumpf and Maurer.[15] Both the behavior of the purely physical gas solubility as well as the salting-out effect are in accordance with the results from previous investigations of the solubility of carbon dioxide in aqueous solutions of several strong electrolytes (for example, Na_2SO_4, NaCl, $(NH_4)_2SO_4$, NH_4Cl; see Rumpf et al.).[15,24,25]

(b) System (CO_2 + K_2CO_3 + H_2O). The solubility of carbon dioxide in aqueous solutions of potassium carbonate was investigated at stoichiometric molalities of the strong electrolyte $\bar{m}_{K_2CO_3} \approx$ (0.43 and 1.7) mol·(kg of water)$^{-1}$ (stoichiometric mass fraction of the salt $\bar{w}_{K_2CO_3} \approx 0.056$ and 0.19, respectively), which correspond to stoichiometric molalities of potassium hydroxide of $\bar{m}^{*}_{KOH} \approx$ (0.86 and 3.5) mol·(kg of water)$^{-1}$. The temperatures were about (313, 353, and 393) K and the solubility pressure reached up to about 9.2 MPa. The experimental results are given in Table 2. Figures 4a and 5a show them plotted as the pressure required to dissolve the carbon dioxide against the gas loading $\bar{m}_{CO_2}/\bar{m}_{K_2CO_3}$ at a preset temperature.

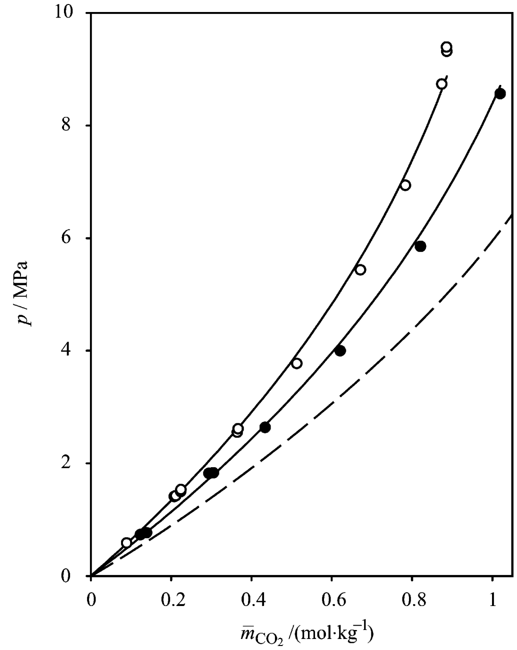

Figure 3. Total pressure above aqueous solutions of (KCl + CO_2) at $T \approx 313.5$ K: ●, $\bar{m}_{KCl} \approx 2$ mol·kg^{-1}; ○, $\bar{m}_{KCl} \approx 4$ mol·kg^{-1}, experimental results; —, correlation results; - - -, correlation results from Rumpf and Maurer[15] for the solubility pressure above the aqueous salt-free solutions.

The vapor pressure behavior is the typical one observed when a sour gas is dissolved in an aqueous solution of a basic compound. When carbon dioxide is added to an aqueous solution of potassium carbonate, initially the total pressure above the solution (region II, $0 < \bar{m}_{CO_2}/\bar{m}_{K_2CO_3} < 1$) only slightly deviates from the vapor pressure above the liquid mixture of (K_2CO_3 + H_2O), because the volatile gas is almost completely chemically absorbed (see reaction II and Figure 1). However, when most potassium carbonate has reacted (region III, $\bar{m}_{CO_2}/\bar{m}_{K_2CO_3} > 1$), carbon dioxide becomes more and more physically dissolved, leading to a steep increase of the total pressure. Furthermore, at fixed pressure and stoichiometric molality of potassium carbonate, the solubility of CO_2 in (K_2CO_3 + H_2O) decreases

Table 2. Experimental Results for the Total Pressure above Aqueous Solutions of Potassium Carbonate and Carbon Dioxide

T	$\bar{m}_{K_2CO_3}$	$\bar{m}_{CO_2}$	p
K	mol·kg^{-1}	mol·kg^{-1}	MPa
313.2	0.4272[a]	0.4992	0.4299
313.25		0.6252	1.029
313.2		0.6894	1.450
313.2		0.8272	2.224
313.2		0.9993	3.373
313.2		1.2549	5.362
313.2		1.5340	8.980
353.1	0.4292[b]	0.4637	0.490
353.1		0.5233	0.9141
353.1		0.6471	2.227
354.15		0.6472	2.256
353.1		0.8926	4.936
353.1		0.9073	5.091
353.1		1.0394	7.091
353.1		1.1086	8.193
393.15	0.4272[a]	0.3650	0.2702
393.2		0.4304	0.4898
393.2		0.4714	0.870
393.2		0.5016	1.272
393.2		0.6076	2.622
393.15		0.7316	4.258
393.2		0.7795	4.941
393.2		1.0437	9.237
313.75	1.7125[c]	1.7371	0.329
313.75		2.0071	2.043
313.85		1.9861	1.914
313.85		2.1441	3.330
313.9		2.3362	5.484
313.75		2.5123	7.700
353.05	1.7125[c]	1.7233	0.7683
353.0		1.8276	1.667
353.05		1.8391	1.831
353.05		1.9080	2.564
353.05		2.0240	4.642
353.0		2.1549	6.672
393.0	1.7125[c]	1.1683	0.2672
393.05		1.5977	0.6854
393.05		1.7174	1.317
393.05		1.7148	1.463
393.0		1.9024	4.174
393.0		2.0205	6.376

[a] $\bar{w}_{K_2CO_3} = 0.05575$. [b] $\bar{w}_{K_2CO_3} = 0.05599$. [c] $\bar{w}_{K_2CO_3} = 0.19138$.

with rising temperature. For example, at $p = 6$ MPa, $\bar{m}_{K_2CO_3} \approx 0.43$ mol·kg^{-1}, and $T \approx (313, 353, \text{and } 393)$ K, the solubility of carbon dioxide amounts to $\bar{m}_{CO_2} \approx (1.34, 0.97, \text{and } 0.85)$ mol·kg^{-1}, respectively.

Correlation of the Gas Solubility

The reference state for the chemical potential of the solvent water is chosen to be the pure liquid at systems temperature and pressure, whereas for the chemical potential of a solute species (carbon dioxide and all ionic species present) it is the one molal solution of that solute in pure water at the temperature and pressure of the system, the solute experiencing the same interactions as if infinitely diluted in pure water. The VLE condition thereby results in the extended Henry's law for carbon dioxide:

$$k_{H,CO_2} \exp\left[\frac{\upsilon^{\infty}_{CO_2}(p - p^{s}_{W})}{RT}\right] a_{CO_2} = y_{CO_2} p \phi_{CO_2} \qquad (1)$$

and in the extended Raoult's law for water:

$$p^{s}_{W} \phi^{s}_{W} \exp\left[\frac{\upsilon_{W}(p - p^{s}_{W})}{RT}\right] a_{W} = y_{W} p \phi_{W} \qquad (2)$$

From these two equations, the total pressure p and the vapor-phase composition (y_i is the vapor-phase mole fraction of component i) are calculated. $k_{H,CO_2}(T)$ is Henry's constant of carbon dioxide in pure water (based on the molality scale) at the vapor pressure of pure water $\{p^{s}_{W}(T)\}$. Correlation equations for these two properties were adopted from Rumpf and Maurer[15] and Saul and Wagner,[26] respectively. The molar volume of liquid water, $\upsilon_W(T, p)$, was approximated by the molar volume of saturated liquid water, $\upsilon^{s}_{W}(T)$, which was also taken from Saul and Wagner.[26] The partial molar volume of carbon dioxide infinitely diluted in water, $\upsilon^{\infty}_{CO_2}(T)$, was calculated as recommended by Brelvi and O'Connell[27] (see also ref 28). R is the universal gas constant.

The virial equation of state, which was truncated after the second virial coefficient, was used to calculate the vapor-phase fugacity coefficients of component i (ϕ_i) and of pure and saturated gaseous water (ϕ^{s}_{W}). Pure component second virial coefficients B_{CO_2,CO_2} and $B_{W,W}$ were calculated from a correlation based on data recommended by Dymond and Smith.[29] The mixed second virial coefficient $B_{CO_2,W}$ was calculated as recommended by Hayden and O'Connell.[30] Details on the calculation of all required second virial coefficients were given previously.[28]

Activities are calculated from Pitzer's molality scale-based equation for the excess Gibbs energy (G^{E}) of aqueous electrolyte solutions[22, 23] (see Appendix 2). The activity of a solute species i follows from

$$a_i = \frac{m_i}{m^{\circ}} \gamma_i \qquad (3)$$

where m_i is the (true) molality of solute species i ($m^{\circ} = 1$ mol·kg^{-1}):

$$\frac{m_i}{m^{\circ}} = \frac{n_i}{M^{*}_{W} n_W} \qquad (4)$$

where n_i is the (true) number of moles of species i, M^{*}_{W} is the relative molar mass of water divided by 1000 ($M^{*}_{W} = 0.01801528$), and n_W is the (true) number of moles of water. The activity coefficient of a solute species γ_i (on the molality scale) is directly calculated from the G^{E} equation, whereas the activity of the solvent water a_W is calculated from the activity coefficients of all solute species by applying the Gibbs−Duhem equation.

As already mentioned in previous work,[31−34] when Pitzer's G^{E} equation is applied to chemical reacting systems, it is much easier to use the general equations for the activity coefficient of a solute species and for the activity of water as a function of the interaction parameters $\beta^{(0)}_{ij}$, $\beta^{(1)}_{ij}$, $\beta^{(2)}_{ij}$, and μ_{ijk}, rather than using rearranged equations as a function of comprehensive parameters (e.g., C^{ϕ}_{MX}, $B^{(0)}_{G,MX}$, $\Gamma_{G,MX,MX}$, $\Gamma_{G,G,MX}$, see Appendix 2). This does not increase the number of independent parameters but greatly simplifies the computer codes. Such a procedure was also applied in the present work.

System ($CO_2 + KCl + H_2O$). Potassium chloride—as a strong electrolyte—is assumed to completely dissociate in liquid water within the temperature and concentration ranges discussed here, that is, well below the solubility limit of the salt in water.[12] Furthermore, when carbon dioxide is dissolved in an aqueous solution of potassium chloride (again within the temperature and concentration ranges discussed here), the dissociation of carbon dioxide in the liquid phase can be neglected.[15,25]

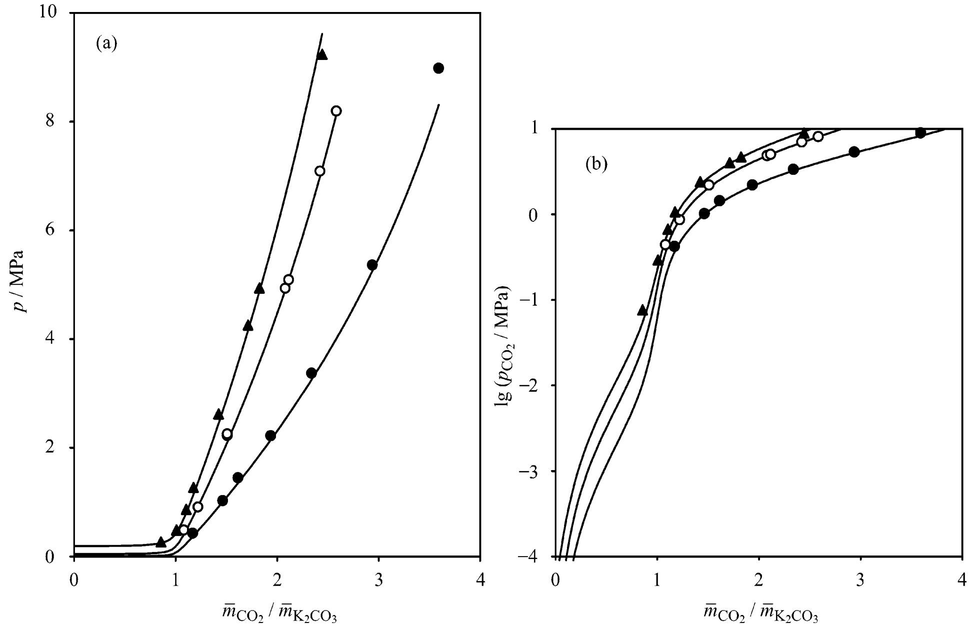

Figure 4. Total pressure (a) and partial pressure of carbon dioxide (b) above aqueous solutions of (K_2CO_3 + CO_2) {$\bar{m}_{K_2CO_3} \approx 0.428$ mol·kg^{-1} ($\bar{w}_{K_2CO_3} \approx 0.0557$) }: ●, $T \approx 313.2$ K; ○, $T \approx 353.1$ K; ▲, $T \approx 393.2$ K, experimental results; —, prediction results. The "experimental result" for the partial pressure of carbon dioxide was calculated from the experimental result for the total pressure by subtracting the partial pressure of water, as predicted by the model.

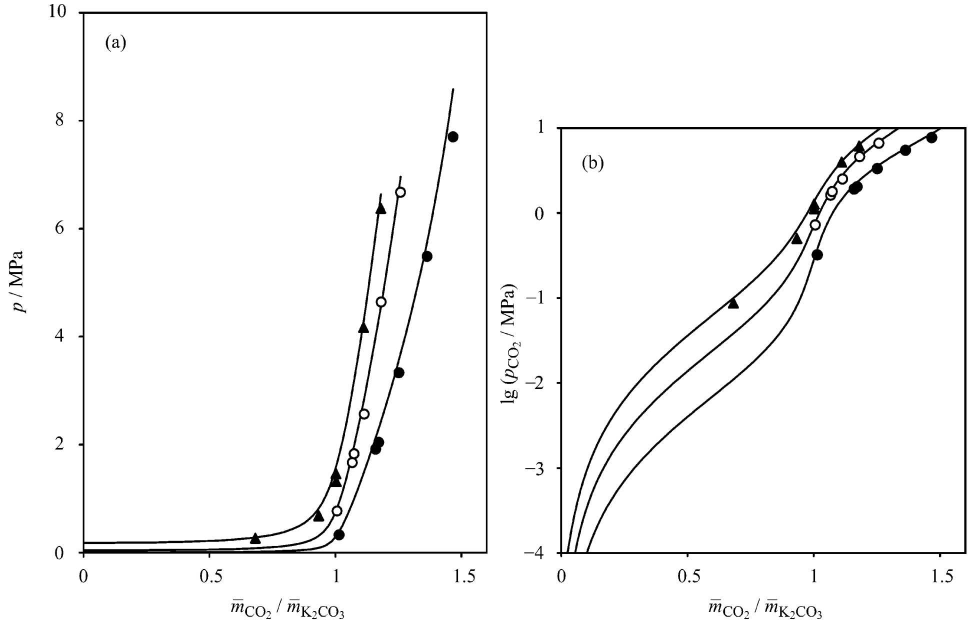

Figure 5. Total pressure (a) and partial pressure of carbon dioxide (b) above aqueous solutions of (K_2CO_3 + CO_2) {$\bar{m}_{K_2CO_3} = 1.7125$ mol·kg^{-1} ($\bar{w}_{K_2CO_3} = 0.19138$)}: ●, $T \approx 313.8$ K; ○, $T \approx 353$ K; ▲, $T \approx 393$ K, experimental results; —, prediction results. The partial pressure of carbon dioxide was calculated from the experimental result for the total pressure by subtracting the partial pressure of water, as predicted by the model.

(a) Interaction Parameters in Pitzer's G^E Model. (i) System (CO_2 + H_2O). Following Rumpf and Maurer,[15] the interaction parameters $\beta^{(0)}_{CO_2,CO_2}$ and μ_{CO_2,CO_2,CO_2} were set to zero. Rumpf and Maurer's correlation of the solubility of carbon dioxide in water covers a temperature range from about (273 to 413) K and is applicable for pressures well beyond 10 MPa.

(ii) System (KCl + H_2O). Parameters describing interactions between potassium and chloride ions in water ($\beta^{(0)}_{K^+,Cl^-}$, $\beta^{(1)}_{K^+,Cl^-}$, and C^{ϕ}_{KCl}) were adopted from Holmes and Mesmer[35] (see also Pitzer).[36] They are valid for temperatures from about (273 to 523) K and up to the solubility limit of the salt,[12] as long as the salt molality does not exceed 6 mol·kg^{-1}. According to the explanations given in Appendix 2, μ_{K^+,Cl^-,Cl^-} was set to zero, and μ_{K^+,K^+,Cl^-} was calculated from

$$\mu_{K+,K+,Cl-} = \frac{1}{3} C^{\phi}_{KCl} \tag{5}$$

To facilitate direct programing, the correlation equations for all Pitzer's interaction parameters used in the present work (which are not equal to zero) are listed in Appendix 3.

(iii) System (CO_2 + KCl + H_2O). Parameters describing interactions between carbon dioxide and potassium chloride in water ($B^{(0)}_{CO_2,KCl}$, $\Gamma_{CO_2,KCl,KCl}$, and $\Gamma_{CO_2,CO_2,KCl}$) were fit to the new experimental results for the solubility of carbon dioxide in aqueous solutions of potassium chloride. Again following to the explanations given in Appendix 2, in the computer codes, the parameters $\beta^{(0)}_{CO_2,Cl^-}$, μ_{CO_2,K^+,K^+}, μ_{CO_2,Cl^-,Cl^-}, and μ_{CO_2,CO_2,Cl^-} were all set to zero arbitrarily. Then:

$$B^{(0)}_{CO_2,KCl} = \beta^{(0)}_{CO_2,K^+} = 0.49547 - \frac{292.86}{(T/K)} + \frac{49047.9}{(T/K)^2} \tag{6}$$

$$\frac{1}{2}\Gamma_{CO_2,KCl,KCl} = \mu_{CO_2,K^+,Cl^-} = -0.000989 \tag{7}$$

$$\Gamma_{CO_2,CO_2,KCl} = \mu_{CO_2,CO_2,K^+} = -0.039588 + \frac{12.008}{(T/K)} \tag{8}$$

Figure 2 illustrates the very satisfactory agreement between the experimental results (symbols) and the correlation results (curves) for the total pressure above liquid mixtures of (CO_2 + KCl + H_2O). The absolute and relative average deviations between the experimental and calculated results amount to ± 0.06 MPa and ± 1.3 %, respectively.

System ($CO_2 + K_2CO_3 + H_2O$). As already mentioned, when carbon dioxide is dissolved in an aqueous solution of potassium carbonate, three reversible chemical reactions occur: the autoprotolysis of water

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \tag{III}$$

and the formation of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-})

$$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq) \tag{IV}$$

$$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq) \tag{V}$$

The condition for chemical equilibrium for a chemical reaction r (= III, IV, and V) is

$$K_r(T) = \prod_i a_i^{\nu_{i,r}} \tag{9}$$

Chemical reaction equilibrium constants (on the molality scale) were adopted from the literature (K_{III} from Edwards et al.,[19] K_{IV} from Patterson et al.,[20] and K_V from Patterson et al.,[21] see also ref 37). The influence of pressure on K_r is neglected. $\nu_{i,r}$ is the stoichiometric factor of reactant i in reaction r ($\nu_{i,r} > 0$ for a product and $\nu_{i,r} < 0$ for an educt).

The balance equation for the amount of substance (the number of moles) of a species i in the liquid solution is

$$n_i = \tilde{n}_i + \sum_r \nu_{i,r}\, \xi_r \tag{10}$$

where ξ_r is the extent of reaction r. Solving this set of equations for a given temperature and stoichiometric amounts (moles) of substances $\tilde{n}_i$ of H_2O, K^+, CO_3^{2-}, and CO_2 gives the “true” composition of the liquid phase (i.e., the amount of substance n_i of all species present).

In addition, in such solutions, the salt potassium bicarbonate may precipitate from the liquid mixture (see, e.g., Benson et al.):[1]

$$KHCO_3(s) \rightleftharpoons K^+(aq) + HCO_3^-(aq) \tag{VI}$$

In the absorption/desorption processes (with or without any activating additives), the deposition of potassium bicarbonate has to be avoided. Hence, it is important to know about the range of conditions where the salt precipitates. Therefore, the model was extended to allow for a deposition of the salt. The phase equilibrium condition yields:

$$K_{sp,KHCO_3}(T) = a_{K^+} a_{HCO_3^-} \tag{11}$$

$K_{sp,KHCO_3}$ is the solubility product for the formation of solid potassium bicarbonate (on the molality scale). The influence of pressure on $K_{sp,KHCO_3}$ is neglected. If the activity product (right-hand side of eq 11) is below the solubility product, potassium bicarbonate will not precipitate from the liquid mixture. Some salt will precipitate only if the solubility product is reached. $K_{sp,KHCO_3}(T)$ was determined in the present work. Details are given below.

(a) Additional Interaction Parameters in Pitzer's G^E Model. (i) System (KOH + H_2O). Because the amount of hydroxide ions dissolved in liquid mixtures of ($CO_2 + K_2CO_3 + H_2O$) is always very small in comparison with the amount of other solute species, parameters describing interactions between potassium and hydroxide ions in water have only a relatively small influence here, even though, they were included in the program files. $\beta^{(0)}_{K^+,OH^-}$, $\beta^{(1)}_{K^+,OH^-}$, and C^{ϕ}_{KOH} were adopted from Pitzer and Mayorga[38] (see also Pitzer).[23, 36] These parameters are strictly only valid at temperatures around 298 K and for potassium hydroxide molalities up to 5.5 mol·kg^{-1}. Again according to the explanations given in Appendix 2, μ_{K^+,OH^-,OH^-} was set to zero, and μ_{K^+,K^+,OH^-} was calculated from

$$\mu_{K^+,K^+,OH^-} = \frac{1}{3} C^{\phi}_{KOH} \tag{12}$$

(ii) System ($K_2CO_3 + H_2O$). First, it is important to know about the solubility of potassium carbonate in water (see Linke and Seidell[12] and Moore et al.[39]). Large amounts of potassium carbonate can be dissolved in water. For example, at T = (298, 323, 348, 373, 398, 423, 448, 473, 498, and 523) K, the molality of K_2CO_3 at saturation in water amounts to about (8.1, 8.8, 9.8, 11.3, 13.6, 16.7, 17.4, 18.1, 18.9, and 19.2) mol·kg^{-1}, respectively. The literature indicates that for 298 K < T < 429 K the stable solid phase is $K_2CO_3 \cdot 1.5H_2O$.[12,39] Above 429 K, a change in the crystal structure was experimentally observed,[39] but the solid phase at this elevated temperature has not been identified yet. Because of the high solubility of potassium carbonate in water, well beyond the salt concentrations that are of interest in connection with the Hot Potassium Carbonate Process and its modifications, it was not necessary to extend the model to account for the deposition of $K_2CO_3 \cdot 1.5H_2O$, etc.

When potassium carbonate is dissolved in pure water, with the exception of very dilute solutions, chemical reactions can be neglected (see Figure 1). Thus, Pitzer's parameters describing interactions between potassium and carbonate ions in water ($\beta^{(0)}_{K^+,CO_3^{2-}}$, $\beta^{(1)}_{K^+,CO_3^{2-}}$, and $C^{\phi}_{K_2CO_3}$) may be straightforwardly determined from experimental results for the VLE of that system. Aseyev's[11] compilation of experimental data for the total pressure above aqueous solutions of potassium carbonate covers wide ranges both in temperature (T = 298 K to 623 K) and in composition {up to $\bar{w}_{K_2CO_3} = 0.5$ ($\bar{m}_{K_2CO_3} \approx 7.2$ mol·kg^{-1}) for T up to 393 K, up to $\bar{w}_{K_2CO_3} = 0.6$ ($\bar{m}_{K_2CO_3} \approx 10.9$ mol·kg^{-1}) for T from (398 to 518) K, up to $\bar{w}_{K_2CO_3} = 0.7$ ($\bar{m}_{K_2CO_3} \approx 16.9$ mol·kg^{-1}) for T from (523 to 568) K, and up to $\bar{w}_{K_2CO_3} = 0.76$ ($\bar{m}_{K_2CO_3} \approx 22.9$ mol·kg^{-1}) for higher temperatures}. Some selected data from Aseyev's compilation {at T = (298, 323, 348, 363, 383, and 398) K, and for stoichiometric mass fractions of the salt up to $\bar{w}_{K_2CO_3} = 0.5$} were used to determine the aforementioned parameters. Again according to the explanations given in Appendix 2, $\mu_{K^+,CO_3^{2-},CO_3^{2-}}$ was set to zero, and

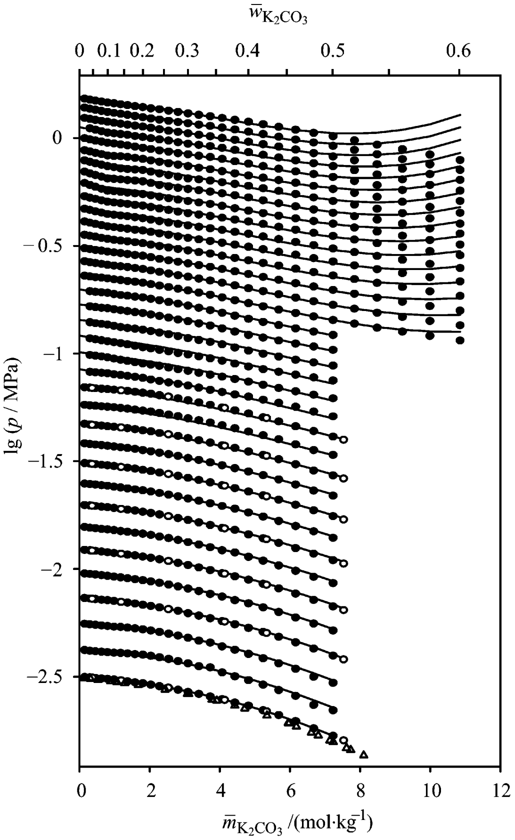

Figure 6. Total pressure above aqueous solutions of K_2CO_3 at T = (298.15 to 473.15) K: ●, experimental data as compiled by Aseyev;[11] ○, experimental data from Puchkov and Kurochkina;[40] △, calculated from isopiestic data by Sarbar et al.[42] (see text); —, correlation/prediction, this work (see text).

$\mu_{K^+,K^+,CO_3{}^{2-}}$ was calculated from

$$\mu_{K^+,K^+,CO_3{}^{2-}} = \frac{\sqrt{2}}{6} C^{\phi}_{K_2CO_3} \tag{13}$$

The resulting parameters are

$$\beta^{(0)}_{K^+,CO_3{}^{2-}} = 0.38621 - \frac{82.857}{(T/K)} \tag{14}$$

$$\beta^{(1)}_{K^+,CO_3{}^{2-}} = 21.975 - \frac{6974.6}{(T/K)} \tag{15}$$

$$\mu_{K^+,K^+,CO_3{}^{2-}} = -0.00872 + \frac{2.69}{(T/K)} \tag{16}$$

As can be seen from Figure 6, the correlation gives a very good description of Aseyev's vapor pressure data (at least up to $\bar{w}_{K_2CO_3}$ = 0.5) for temperatures ranging from 298 K to at least 473 K. In these regions, the relative average deviation between the experimental and calculated results amounts to about ± 1 %. As expected, beyond $\bar{w}_{K_2CO_3}$ = 0.5, the deviation between the experimental and calculated results for the total pressure increases with rising mass fraction of the salt and with rising temperature. However, the concentration and temperature ranges with relatively large deviations between experimental and calculated results are not of interest in connection with the Hot Potassium Carbonate Process and its modifications; therefore, no attempt was made to improve the correlation there.

The experimental data for the total pressure above liquid mixtures of (K_2CO_3 + H_2O) from Puchkov and Kurochkina[40] {measured at temperatures from about 298 K to 363 K and at $\bar{w}_{K_2CO_3}$ up to about 0.51 ($\bar{m}_{K_2CO_3} \approx 7.5$ mol·kg^{-1})} are shown in Figure 6 for comparison. They agree perfectly with Aseyev's data and with the calculated results from the new model (relative average deviation between experimental and calculated results for the pressure ≈ ± 0.7%).

Apelblat[41] reported vapor pressures of water over aqueous solutions of potassium carbonate at temperatures from (283 to 313) K, however, only at saturation (i.e., at high salt concentrations beyond the range of interest). Therefore, these data were not taken into account to determine the pertaining Pitzer parameters.

It may also be interesting to compare the results for the osmotic coefficient of liquid mixtures of (K_2CO_3 + H_2O), resulting from the experimental data for the total pressure by Aseyev[11] and by Puchkov and Kurochkina,[40] with calculation results from the model. Neglecting all chemical reactions to determine the activity of water in the ideal solution, the molality scale-based osmotic coefficient in the system is

$$\phi = -\frac{\ln a_W}{3M^*_W \dfrac{\bar{m}_{K_2CO_3}}{m^\circ}} \tag{17}$$

The activity of water is calculated from the extended Raoult's law by again calculating the fugacity coefficient of pure water in the gaseous phase from the truncated virial equation of state:

$$\ln a_W = (\upsilon_W - B_{W,W}) \frac{\Delta p}{RT} + \ln\left[1 - \frac{\Delta p}{p^s_W}\right] \tag{18}$$

where Δp is the vapor pressure depression arising from the addition of potassium carbonate to pure liquid water:

$$\Delta p = p^s_W - p \tag{19}$$

As expected, but not at all temperatures, the osmotic coefficient data resulting from the total pressure from Aseyev[11] and from Puchkov and Kurochkina[40] agree reasonably with the calculated results from the model (see Figure 7).

Furthermore, Sarbar et al.[42] carried out isopiestic investigations of liquid mixtures of (K_2CO_3 + H_2O) at T = 298.15 K and at $\bar{m}_{K_2CO_3}$ = (0.13 to 8.1) mol·kg^{-1}. As can be seen from Figure 7, the osmotic coefficients resulting from the isopiestic data of Sarbar et al.[42] systematically deviate (in average by about +0.12) from the new correlation. That is, they deviate from the osmotic coefficients resulting from the vapor pressure data by Aseyev.[11] Consequently, the vapor pressure data resulting from the isopiestic data of Sarbar et al.[42] also systematically deviate from the new correlation, by about −0.1 % at the lowest stoichiometric salt molality up to about −5.8 % at one of the highest stoichiometric salt molalities (see Figure 6). The data by Sarbar et al.[42] were therefore excluded from the fitting procedure.

(iii) Systems ($KHCO_3$ + H_2O) and (K_2CO_3 + $KHCO_3$ + H_2O). As explained in Appendix 1, an aqueous solution of potassium bicarbonate is equivalent to an aqueous (stoichiometrically) equimolar solution of carbon dioxide and potassium carbonate. As can be seen from Figure 1, in such a solution chemical reactions III to V cannot be neglected, and the solution contains appreciable amounts of carbon dioxide in molecular form. Hence, Pitzer's parameters involving the species carbon dioxide may play an essential role here. It is therefore not recommended to determine the relevant Pitzer's parameters for interactions between potassium and bicarbonate in water from

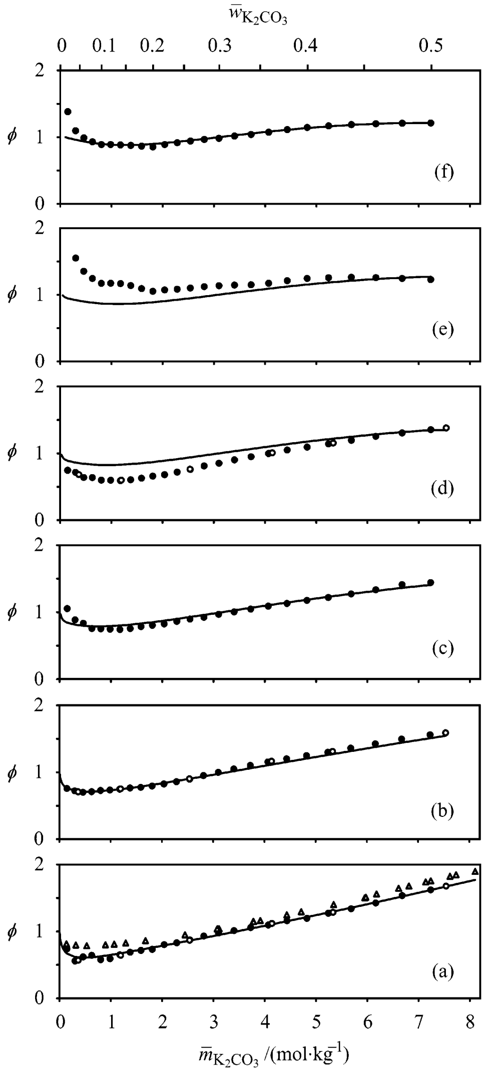

Figure 7. Molality scale-based osmotic coefficient of aqueous solutions of potassium carbonate $\phi = \ln a_W/\{-3M^*_W(\bar{m}_{K_2CO_3}/m°)\}$ at constant temperature: a, T = 298.15 K; b, T = 323.15 K; c, T = 348.15 K; d, T = 363.15 K; e, T = 383.15 K; f, T = 398.15 K. ●, ○ evaluated from experimental data for the total pressure above ($K_2CO_3 + H_2O$) as compiled by Aseyev[11] and from Puchkov and Kurochkina,[40] respectively (see text). △, calculated from isopiestic data by Sarbar et al.[42] (see text); —, correlation/prediction, this work (see text).

VLE data for the system ($KHCO_3 + H_2O$). However, in aqueous solutions of carbon dioxide and potassium carbonate, and at gas loadings $\bar{m}_{CO_2}/\bar{m}_{K_2CO_3}$ well below 1, carbon dioxide is almost completely converted to bicarbonate. Here, following Appendix 2, only parameters describing interactions between potassium and carbonate ($\beta^{(0)}_{K^+,CO_3^{2-}}$, $\beta^{(1)}_{K^+,CO_3^{2-}}$, and $C^{\phi}_{K_2CO_3}$), which were already determined as described above, as well as between potassium and bicarbonate ($\beta^{(0)}_{K^+,HCO_3^-}$, $\beta^{(1)}_{K^+,HCO_3^-}$, and $C^{\phi}_{KHCO_3}$), and in principle also between potassium, carbonate, and bicarbonate ($\mu_{K^+,CO_3^{2-},HCO_3^-}$) are important.

Three attempts were made to determine the missing parameters. In a first attempt, $\mu_{K^+,CO_3^{2-},HCO_3^-}$ was set to zero, and only ($\beta^{(0)}_{K^+,HCO_3^-}$, $\beta^{(1)}_{K^+,HCO_3^-}$, and $C^{\phi}_{KHCO_3}$) were fit to the data base for the partial pressure of carbon dioxide (p_{CO_2}) above liquid mixtures of ($CO_2 + K_2CO_3 + H_2O$) by Tosh et al.[3] In that investigation, $T \approx$ (343 to 413) K, $\bar{w}_{K_2CO_3}$ = 0.2, 0.3, and 0.4 $\{\bar{m}_{K_2CO_3} \approx$ (1.8, 3.1, and 4.8) mol·kg$^{-1}\}$, $\bar{m}_{CO_2}/\bar{m}_{K_2CO_3} \approx$ 0.1 to 0.87, and p_{CO_2} amounts up to about 0.92 MPa. The influence of temperature on these parameters was described by means of the common equation, $f(T) = a + b/(T/\text{K})$. The model satisfactorily represented the data. The average relative deviation between the experimental and the correlation results for p_{CO_2} amounted to ± 11.1 % over the entire range of conditions (± 8.7 %, ± 9 %, and ± 13.3 % at $\bar{w}_{K_2CO_3}$ = 0.2, 0.3, and 0.4, respectively). It might be noted, that no appreciable improvement was achieved by taking additionally into account the parameter $\mu_{K^+,CO_3^{2-},HCO_3^-}$ in the correlation (cf., Chen et al.[43]). Next, some literature data for the solubility of potassium bicarbonate in aqueous solutions of the stoichiometric components carbon dioxide and potassium carbonate (all data are, however, within region II) were considered: the data compiled included that of Seidell and Linke[12] {for systems $KHCO_3 + H_2O$ (273 K < T < 343 K) and $K_2CO_3 + KHCO_3 + H_2O$ (278 K < T < 323 K)}, Hill and Hill[13] {for system $K_2CO_3 + KHCO_3 + H_2O$ (298 K < T < 309 K)}, and Benson et al.[1] {for system $K_2CO_3 + KHCO_3 + H_2O$ (301.9 K < T < 415.4 K)}. The solubility data reported by Lyudkovskaya et al.,[44] for the system $K_2CO_3 + KHCO_3 + H_2O$ (301.9 K < T < 415.4 K), are not in accordance with the data of Benson et al.[1] and were therefore discarded. By applying the model with the new parameters, the solubility product of potassium bicarbonate $K_{sp,KHCO_3}$ was calculated from the saturation data[1,12,13] at the different temperatures. However, a large scattering was observed in the calculated values, and it was not possible to correlate the results by only considering the influence of temperature on $K_{sp,KHCO_3}$.

In a second attempt, $\mu_{K^+,CO_3^{2-},HCO_3^-}$ again was set to zero, and ($\beta^{(0)}_{K^+,HCO_3^-}$, $\beta^{(1)}_{K^+,HCO_3^-}$, $C^{\phi}_{KHCO_3}$) as well as $K_{sp,KHCO_3}$ were simultaneously adjusted to both the VLE data (p_{CO_2}) by Tosh et al.[3] and the SLE data by Benson et al.,[1] Seidell and Linke,[12] and Hill and Hill.[13] The influence of temperature on all these parameters (including $\ln K_{sp,KHCO_3}$) was again described by $f(T) = a + b/(T/\text{K})$. However, this procedure resulted in a much worse description of the VLE data and in a barely appreciable improvement in the representation of the SLE data.

Last, in a third and successful attempt, $\mu_{K^+,CO_3^{2-},HCO_3^-}$ was taken into account as well: $\mu_{K^+,CO_3^{2-},HCO_3^-}$, ($\beta^{(0)}_{K^+,HCO_3^-}$, $\beta^{(1)}_{K^+,HCO_3^-}$, $C^{\phi}_{KHCO_3}$), and $K_{sp,KHCO_3}$ were simultaneously adjusted to both the VLE and the SLE data mentioned before. The influence of temperature on all these parameters (including $\ln K_{sp,KHCO_3}$) was again described by $f(T) = a + b/(T/\text{K})$. In addition, according to the explanations given in Appendix 2, in the program codes $\mu_{K^+,HCO_3^-,HCO_3^-}$ was set to zero, and μ_{K^+,K^+,HCO_3^-} was calculated from

$$\mu_{K^+,K^+,HCO_3^-} = \frac{1}{3}C^{\phi}_{KHCO_3} \qquad (20)$$

The resulting parameters are

$$\beta^{(0)}_{K^+,HCO_3^-} = 0.10662 - \frac{40.439}{(T/\text{K})} \qquad (21)$$

$$\beta^{(1)}_{K^+,HCO_3^-} = 8.19 - \frac{2648}{(T/\text{K})} \qquad (22)$$

$$\mu_{K^+,K^+,HCO_3^-} = -0.000348 + \frac{0.215}{(T/\text{K})} \qquad (23)$$

$$\mu_{K^+,CO_3^{2-},HCO_3^-} = -0.0000118 - \frac{0.2181}{(T/\text{K})} \qquad (24)$$

$$\ln K_{sp,KHCO_3} = 16.1646 - \frac{4974.48}{(T/\text{K})} \qquad (25)$$

The model then resulted in a very reasonable description of both the VLE data[3] and the SLE data.[1,12,13] The average relative

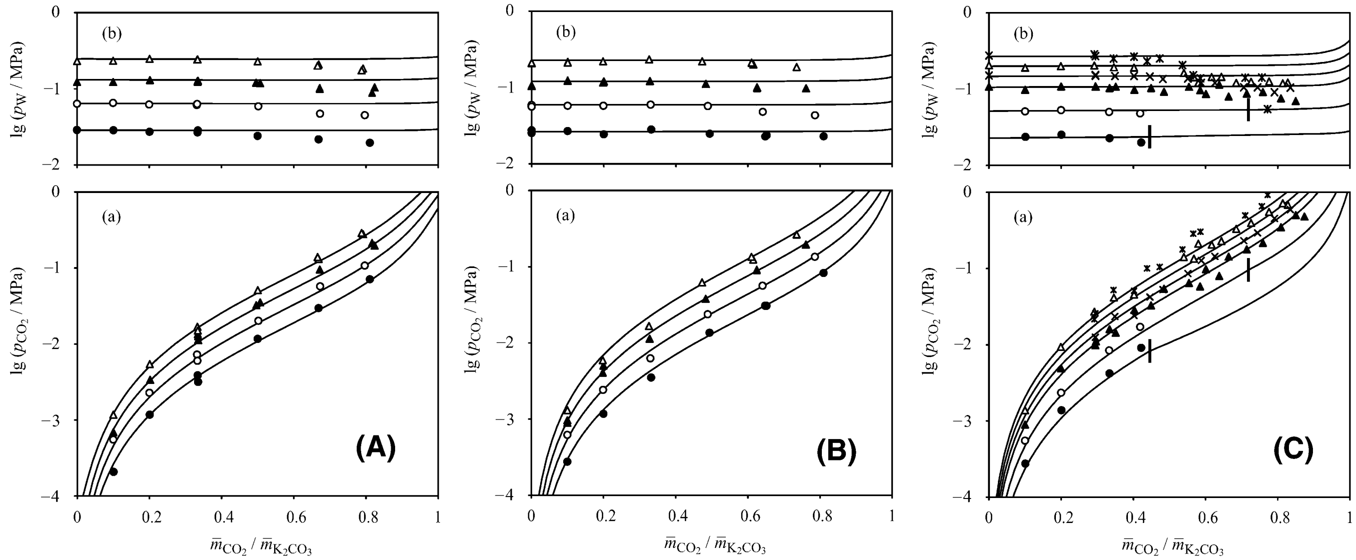

Figure 8. Partial pressures of carbon dioxide (a) and water (b) above aqueous solutions of carbon dioxide and potassium carbonate at preset temperature and gas-free liquid-phase composition {(A) $\bar{w}_{K_2CO_3} = 0.2$ ($\bar{m}_{K_2CO_3} \approx 1.809$ mol·kg^{-1}); (B) $\bar{w}_{K_2CO_3} = 0.3$ ($\bar{m}_{K_2CO_3} \approx 3.101$ mol·kg^{-1}); (C) $\bar{w}_{K_2CO_3} = 0.4$ ($\bar{m}_{K_2CO_3} \approx 4.824$ mol·kg^{-1})}. Symbols = experimental data from Tosh et al.[3] (●, T = 343.15 K; ○, T = 363.15 K; ▲, T = 383.15 K; ×, T = 393.15 K; △, T = 403.15 K; ∗, T = 413.15 K). —, correlation for p_{CO_2}; prediction for p_W, this work.

deviation between the experimental results for the partial pressure of carbon dioxide from Tosh et al.[3] and the calculated results amounts to ± 12.2 % over the entire range of conditions (± 10 %, ± 9.2 %, and ± 14.7 % at $\bar{w}_{K_2CO_3} = 0.2$, 0.3, and 0.4, respectively). In Figure 8, the experimental data for the partial pressure of carbon dioxide p_{CO_2} (and water p_W) from Tosh et al.[3] are plotted against the gas loading $\bar{m}_{CO_2}/\bar{m}_{K_2CO_3}$ at preset temperature and gas-free liquid-phase composition $\bar{w}_{K_2CO_3} = 0.2$, 0.3, and 0.4 {$\bar{m}_{K_2CO_3} \approx$ (1.8, 3.1, and 4.8) mol·kg^{-1}}, respectively. The curves in the figure represent the correlation results for p_{CO_2} and the prediction results for p_W. Within the whole range of conditions investigated by Tosh et al.,[3] and in accordance with the experiment, no precipitation of potassium bicarbonate is predicted by the model. The vertical bars in Figure 8C denote the predictions of the model for the limit, at which addition of more carbon dioxide to the aqueous solution of carbon dioxide and potassium carbonate with $\bar{w}_{K_2CO_3} = 0.4$ result in a deposition of potassium bicarbonate.

In Figure 9, the solubility product of potassium bicarbonate in water is plotted against the temperature. The solid line represents the present correlation (eq 25). Symbols denote the numerical values for ln ($a_{K^+}a_{HCO_3^-}$) of the saturated liquid mixture calculated from Pitzer's model (with the given interaction parameters) at temperatures and compositions reported in refs 1, 12, and 13. To allow for a quantitative comparison between the experimental and calculated results at saturation, the potassium bicarbonate saturation temperature was calculated from the present model at a preset liquid-phase composition and compared with the aforementioned data[1,12,13] (see Figure 10). Over the entire range of conditions, the average absolute deviation between the experimental and calculated temperatures amounts to about ± 3 K.

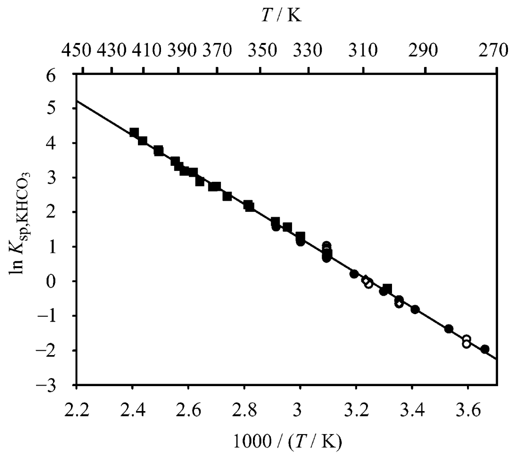

Figure 9. Solubility product of potassium bicarbonate in water (ln $K_{sp,KHCO_3}$) plotted against the temperature. The solid line denotes correlation results for ln $K_{sp,KHCO_3}$ according to eq 25, this work (see text). Symbols denote results from the model presented here for ln ($a_{K^+}a_{HCO_3^-}$) calculated from saturation data from different sources: ●, compilation by Seidell and Linke[12] (system $KHCO_3 + H_2O$); ○, compilation by Seidell and Linke[12] (system $K_2CO_3 + KHCO_3 + H_2O$); ◇, Hill and Hill[13] (system $K_2CO_3 + KHCO_3 + H_2O$); ■, Benson et al.[1] (system $K_2CO_3 + KHCO_3 + H_2O$).

It might be noted, that Roy et al.[45] reported a set of Pitzer parameters ($\beta^{(0)}_{K^+,CO_3^{2-}}$, $\beta^{(1)}_{K^+,CO_3^{2-}}$, $C^{\phi}_{K_2CO_3}$), ($\beta^{(0)}_{K^+,HCO_3^-}$, $\beta^{(1)}_{K^+,HCO_3^-}$, $C^{\phi}_{KHCO_3}$), $\beta^{(0)}_{CO_3^{2-},HCO_3^-}$, $\mu_{K^+,CO_3^{2-},HCO_3^-}$ (and $\beta^{(0)}_{CO_3^{2-},Cl^-}$, μ_{K^+,CO_3^{2-},Cl^-}, μ_{K^+,HCO_3^-,Cl^-}), which might have been adopted here (the correlation by Roy et al.[45] does not include unsymmetrical mixing terms in Pitzer's equation). That set was adjusted by those authors to the isopiestic data for the system ($K_2CO_3 + H_2O$) given by Sarbar et al.,[42] to their earlier electromotive force (emf) data in aqueous mixtures of $KHCO_3$, KCl, and CO_2,[46] and to their emf data in aqueous mixtures of K_2CO_3, $KHCO_3$, and KCl.[45] These investigations cover a temperature range from (278 to 318) K. Applying that parameter set leads to considerably larger deviations between experimental results and calculated (i.e., *predicted*) results for both the total pressure above liquid mixtures of ($K_2CO_3 + H_2O$)[11,40] and for the partial pressure of carbon dioxide above liquid mixtures of ($CO_2 + K_2CO_3 + H_2O$) in the low gas loading region[4] than the correlation presented here. Some other sets of parameters for those systems were provided by Roy et al.[45] and by Simonson et al.[47] In particular, Simonson et al.[47] extended the temperature range up to 368 K by considering some additional emf data in aqueous mixtures of $KHCO_3$, KCl, and CO_2. These parameter sets could not be tested here, because in these correlations unsymmetrical mixing terms were included in Pitzer's equation. Because the liquid mixtures investigated by Roy et al.[45,46] and

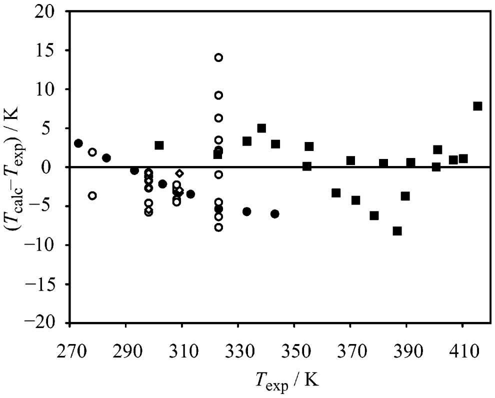

Figure 10. ($T_{calc} - T_{exp}$) plotted against T_{exp}, where T is the potassium bicarbonate saturation temperature at preset liquid-phase composition. (Subscripts exp and calc denote experimental data and calculation results from the present model, respectively.) ●, compilation by Seidell and Linke[12] (system $KHCO_3 + H_2O$); ○, compilation by Seidell and Linke[12] (system $K_2CO_3 + KHCO_3 + H_2O$); ◇, Hill and Hill[13] (system $K_2CO_3 + KHCO_3 + H_2O$); ■, Benson et al.[1] (system $K_2CO_3 + KHCO_3 + H_2O$).

by Simonson et al.[47] contained considerable amounts of potassium chloride, these emf data were not included in the fitting runs in the present work.

(iv) Systems ($CO_2 + K_2CO_3 + H_2O$) and ($CO_2 + KHCO_3 + H_2O$). In the thermodynamic model used to describe the solubility of carbon dioxide in aqueous solutions of potassium carbonate, Pitzer's parameters for interactions between carbon dioxide and potassium carbonate ($B^{(0)}_{CO_2,K_2CO_3}$, $\Gamma_{CO_2,K_2CO_3,K_2CO_3}$, and $\Gamma_{CO_2,CO_2,K_2CO_3}$) as well as between carbon dioxide and potassium bicarbonate ($B^{(0)}_{CO_2,KHCO_3}$, $\Gamma_{CO_2,KHCO_3,KHCO_3}$, and $\Gamma_{CO_2,CO_2,KHCO_3}$) are still lacking. As can be seen from Figure 1, at very high gas loadings well beyond $\bar{m}_{CO_2}/\bar{m}_{K_2CO_3} = 1$, only the species potassium, bicarbonate, and carbon dioxide appear in appreciable amounts, whereas at gas loadings around 1, carbonate appears in a smaller amount as well. Therefore, to determine the mentioned parameters one may use gas solubility data in those areas. However, in particular within the temperature and gas-free liquid-phase composition ranges which are of importance in connection with the Hot Potassium Carbonate Process ($343\ \mathrm{K} < T < 413\ \mathrm{K}$, $0.2 < \bar{w}_{K_2CO_3} < 0.4$, i.e., $1.8\ \mathrm{mol \cdot kg^{-1}} < \bar{m}_{K_2CO_3} < 4.8\ \mathrm{mol \cdot kg^{-1}}$), no such experimental information was found in the open literature.

Therefore, a more or less pragmatic approach is accomplished here: Pitzer's parameters for interactions between carbon dioxide and potassium ions ($\beta^{(0)}_{CO_2,K^+}$, μ_{CO_2,CO_2,K^+}, and μ_{CO_2,K^+,K^+}), which had already been fixed previously (the first two according to eqs 6 and 8, the latter was set to zero), are adopted here. As described previously, these parameters are based on the solubility pressures above liquid mixtures of ($CO_2 + KCl + H_2O$) from the present work and are thereby valid for temperatures from (313 to 433) K, so they cover the relevant temperature range for the Hot Potassium Carbonate Process. All other missing parameters (that is, $\beta^{(0)}_{CO_2,CO_3^{2-}}$, $\beta^{(0)}_{CO_2,HCO_3^-}$, $\mu_{CO_2,K^+,CO_3^{2-}}$, $\mu_{CO_2,CO_3^{2-},CO_3^{2-}}$, μ_{CO_2,K^+,HCO_3^-}, $\mu_{CO_2,HCO_3^-,HCO_3^-}$, $\mu_{CO_2,CO_2,CO_3^{2-}}$, and μ_{CO_2,CO_2,HCO_3^-}) are set to zero. This results in (cf. Appendix 2):

$$B^{(0)}_{CO_2,K_2CO_3} = 2\beta^{(0)}_{CO_2,K^+} \qquad (26)$$

$$\Gamma_{CO_2,K_2CO_3,K_2CO_3} = 0 \qquad (27)$$

$$\Gamma_{CO_2,CO_2,K_2CO_3} = 2\mu_{CO_2,CO_2,K^+} \qquad (28)$$

and

$$B^{(0)}_{CO_2,KHCO_3} = \beta^{(0)}_{CO_2,K^+} \qquad (29)$$

$$\Gamma_{CO_2,KHCO_3,KHCO_3} = 0 \qquad (30)$$

$$\Gamma_{CO_2,CO_2,KHCO_3} = \mu_{CO_2,CO_2,K^+} \qquad (31)$$

Thus, by simply including $\beta^{(0)}_{CO_2,K^+}$ and μ_{CO_2,CO_2,K^+} (according to eqs 6 and 8) for calculating the VLE of the system ($CO_2 + K_2CO_3 + H_2O$), the model allows for predictions of the carbon dioxide solubility pressure in the higher gas loading ranges. Calculated results may be checked by comparison with the few experimental results for the gas solubility reported in the present work. As can be seen from Figures 4a and 5a, the quality of these predictions is remarkable. The average absolute deviation between the experimental results for the total pressure and the prediction results amounts to ± 0.16 MPa over the entire range of conditions (± 0.12 MPa and ± 0.21 MPa at $\bar{w}_{K_2CO_3} \approx 0.056$ and 0.19, respectively). If $\beta^{(0)}_{CO_2,K^+}$ and μ_{CO_2,CO_2,K^+} are set to zero, those deviations amount to ± 0.67 MPa (± 0.46 MPa and ± 0.93 MPa, respectively). Figures 4b and 5b also illustrate the good agreement between the partial pressure of carbon dioxide as calculated from the experimental total pressures by subtracting the partial pressure of water (as predicted by the model) and the calculated results from the model.

Comparison with Literature Data

System ($CO_2 + KCl + H_2O$). Table 3 reports average relative and absolute deviations between experimental results for the total pressure and the partial pressure of carbon dioxide above liquid mixtures of ($CO_2 + KCl + H_2O$) taken from the literature as well as from the present work and correlation/prediction results from the present model. The experimental ranges for the temperature, the stoichiometric molalities of potassium chloride and carbon dioxide, and the total pressure or the partial pressure of carbon dioxide of all the investigations are also given in Table 3. The data by Markham and Kobe[48] (which were taken solely at $p_{CO_2} = 1$ atm) and by Yasunishi and Yoshida[49] (which were taken only at $p = 1$ atm) agree very well with calculated results from the new model (that is, they agree with the new experimental results). However, the data by Kiepe et al.,[50] which were taken at pressures up to 10.5 MPa, widely differ from the results calculated by the model {in average by 0.53 MPa [12.1 %]}. That indicates that the data by Kiepe et al.[50] severely disagree with the new experimental results. In Figure 11, both the experimental data (symbols) for the total pressure above aqueous solutions of potassium chloride as reported by Kiepe et al.[50] and the prediction results from the new model (solid curves) are plotted against the molality of carbon dioxide in the liquid (at a preset temperature and at several salt molalities) for comparison. Kiepe et al.[50] also report some experimental results for the solubility pressure above the salt-free system ($CO_2 + H_2O$), which are plotted in Figure 11 as well (only at two temperatures), and which again severely disagree {in average by 0.75 MPa (13.7 %)} with the correlation results from the model by Rumpf and Maurer[15] (broken curves). This model was based on an extensive experimental database from the literature for the solubility of carbon dioxide in water and has been confirmed in a long series of experimental investigations in aqueous solutions of strong and weak electrolytes and in aqueous solutions of organic compounds (see, e.g., refs 15, 16, 24, 25, 28, 33, and 34).

System ($CO_2 + K_2CO_3 + H_2O$). Table 4 lists the average relative and absolute deviations between experimental results

Table 3. Comparison between Experimental Data from the Literature for the Total Pressure and the Partial Pressure of CO_2 above Liquid Mixtures of (CO_2 + KCl + H_2O) and Calculation Results from the Present Model

		experimental ranges					average deviations			
		T	$\bar{m}_{KCl}$	$\bar{m}_{CO_2}$	p	p_{CO_2}	$\lvert\Delta p/p\rvert$	$\lvert\Delta p\rvert$	$\lvert\Delta p_{CO_2}/p_{CO_2}\rvert$	$\lvert\Delta p_{CO_2}\rvert$
source	N[a]	K	mol·kg^{-1}	mol·kg^{-1}	MPa	MPa	%	MPa	%	MPa
Correlation this work	98	313−433	<4.05	<1.02	<9.4		1.3	0.06		
Prediction										
ref 48	16	273−313	<4	<0.076		0.1013			1.6	0.0016
ref 49	16	298−308	<4.8	<0.033	0.1013		1.3	0.0013		
ref 50	88	313−353	<4	<1.24	<10.5		12.1	0.53		

[a] N = number of experimental points.

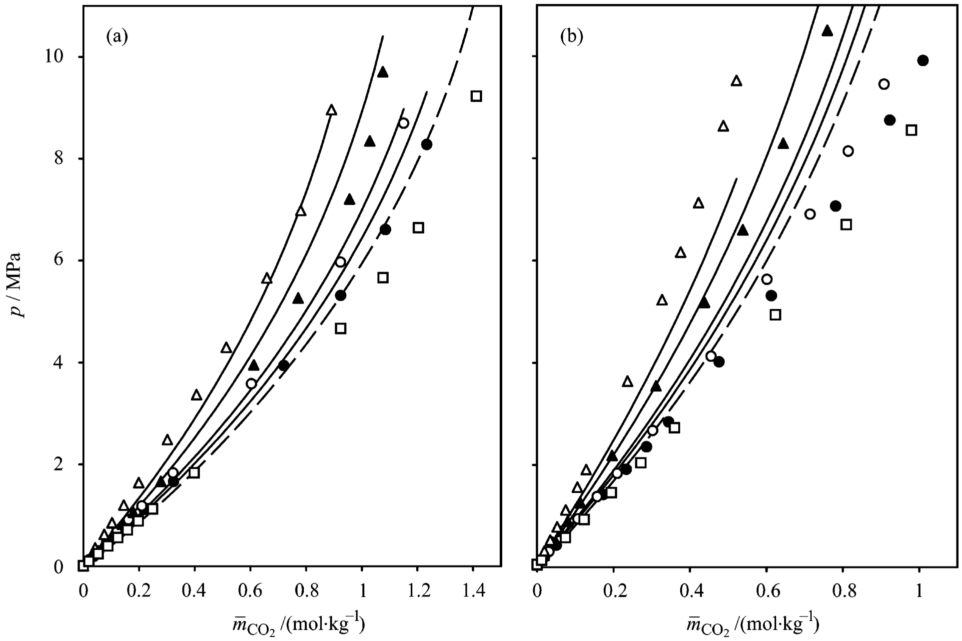

Figure 11. Total pressure above aqueous solutions of (KCl + CO_2) at $T \approx 313.3$ K (a) and at $T \approx 353$ K (b). Symbols = experimental results from Kiepe et al.[50] (□, no salt; ●, $\bar{m}_{KCl}$ = 0.5 mol·kg^{-1}; ○, $\bar{m}_{KCl}$ = 1 mol·kg^{-1}; ▲, $\bar{m}_{KCl}$ = 2.5 mol·kg^{-1}; △, $\bar{m}_{KCl} \approx$ 4 mol·kg^{-1}); —, prediction results (based on experimental data from the present work); - - -, correlation results from Rumpf and Maurer[15] for the solubility pressure above the aqueous salt-free solutions.

Table 4. Comparison between Experimental Data from the Literature for the Total Pressure and the Partial Pressure of CO_2 Above Liquid Mixtures of (CO_2 + K_2CO_3 + H_2O) and Calculation Results from the Present Model

		experimental ranges					average deviations			
		T	$\bar{m}_{K_2CO_3}$	$\bar{m}_{CO_2}$	p	p_{CO_2}	$\lvert\Delta p/p\rvert$	$\lvert\Delta p\rvert$	$\lvert\Delta p_{CO_2}/p_{CO_2}\rvert$	$\lvert\Delta p_{CO_2}\rvert$
source	N[a]	K	mol·kg^{-1}	$\bar{m}_{K_2CO_3}$	MPa	MPa	%	MPa	%	MPa
Correlation ref 3	132	343−413	1.8−4.8	0.1−0.88	<0.98	<0.92	9.8	0.015	12.2	0.015
Prediction										
this work	41	313−393	0.43−1.7	0.7−3.6	0.27−9.2		7	0.16		
ref 52	50	303−370	0.5−1.06	0.51−0.93		<0.084			62	0.01
ref 53	35	298−310	0.0025−0.16	0.23−0.87		≈33 × 10−6			5.9	2 × 10^{-6}
ref 54	9	368	0.049	0.23−0.69		<5 × 10^{-4}			65	1.6 × 10^{-4}
ref 44	52	383−443	3.1−7.2	0.16−0.86	<1.63		14	0.13		
ref 51	65	313−353	1.8−3.1	0.075−0.42		<50 × 10^{-4}			28	2.1 × 10^{-4}
ref 55	28	298−323	0.38−0.8	0.58−1.8		<2.3			35	0.13

[a] N = number of experimental points.

for the total pressure and the partial pressure of carbon dioxide above liquid mixtures of (CO_2 + K_2CO_3 + H_2O) taken from the literature as well as from the present work and correlation/prediction results from the present model. The experimental ranges for the temperature, the stoichiometric molality of potassium carbonate, the gas loading, and the total pressure and/or the partial pressure of carbon dioxide of all the investigations are given as well. The data by Lyudkovskaya et al.[44] and by Korbutova et al.[51] are particularly interesting, because the compositions of many of the aqueous potassium carbonate solutions investigated by those authors were within the ranges which are relevant in connection with the Hot Potassium Carbonate Process and its modifications (1.8 to 4.8 mol·kg^{-1}).

In Figure 12, both the experimental data for the CO_2 partial pressure by Korbutova et al.[51] (symbols) and the calculated results from the new model (curves) are plotted against the gas loading $\bar{m}_{CO_2}/\bar{m}_{K_2CO_3}$ (at a preset temperature and at several molalities of the salt). That investigation covers a temperature

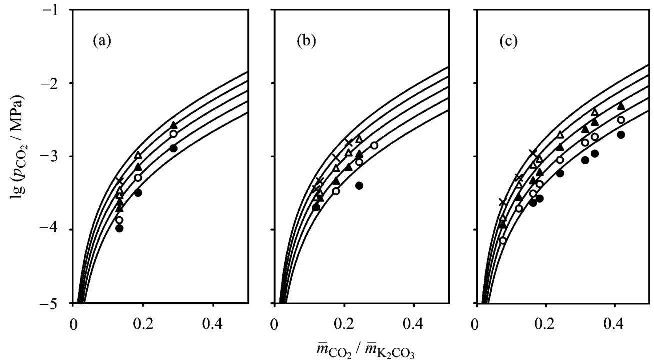

Figure 12. Partial pressure of carbon dioxide above aqueous solutions of carbon dioxide and potassium carbonate at preset temperature and gas-free liquid-phase composition {(a) $\bar{w}_{K_2CO_3} = 0.2$ ($\bar{m}_{K_2CO_3} \approx 1.809$ mol·kg^{-1}), (b) $\bar{w}_{K_2CO_3} = 0.25$ ($\bar{m}_{K_2CO_3} \approx 2.412$ mol·kg^{-1}), (c) $\bar{w}_{K_2CO_3} = 0.3$ ($\bar{m}_{K_2CO_3} \approx 3.101$ mol·kg^{-1})}. Symbols = experimental data from Korbutova et al.[51] (●, $T = 313.15$ K; ○, $T = 323.15$ K; ▲, $T = 333.15$ K; △, $T = 343.15$ K; ×, $T = 353.15$ K); —, prediction, this work.

range from (313 to 353) K. However, the investigated gas loading range was rather low (to 0.42 at a maximum). Under those conditions, the partial pressure of carbon dioxide is rather small (the reported values range up to 5 kPa at a maximum), and overall experimental uncertainties may become large. Nevertheless, as can be seen from Figure 12 (and also from Table 4), the calculated results agree reasonably with the experimental data by Korbutova et al.[51] To extend the new correlation down to 313 K, we also tried to fit the relevant model parameters to simultaneously describe the data from Korbutova et al.[51] and Tosh et al.[4] However, such a procedure did not improve the quality of the correlation.

The investigation by Lyudkovskaya et al.[44] covers a temperature range from (383 to 443) K and a gas loading range from about 0.16 to 0.86. Only experimental results for the total pressure are reported. The partial pressure of carbon dioxide reported in that investigation was calculated by the authors by subtracting the total pressure above the gas free solution from the total pressure above the gas containing solution and is therefore discarded here. In Figure 13, both these experimental data for the total pressure (symbols) and the calculated results from the new model (solid curves) are plotted against the gas loading (at a preset temperature and at several salt molalities). At $\bar{m}_{K_2CO_3} \approx 7.2$ mol·kg^{-1}, $T \approx 393$ K and 413 K, and for $\bar{m}_{CO_2}/\bar{m}_{K_2CO_3} > 0.55$ and 0.72, respectively, a deposition of potassium bicarbonate is predicted by the model. This limit is denoted by the vertical bars in Figure 13. As can be seen from the figure, the experimental results by Lyudkovskaya et al.[44] also agree reasonably (see also Table 4) with the calculated results.

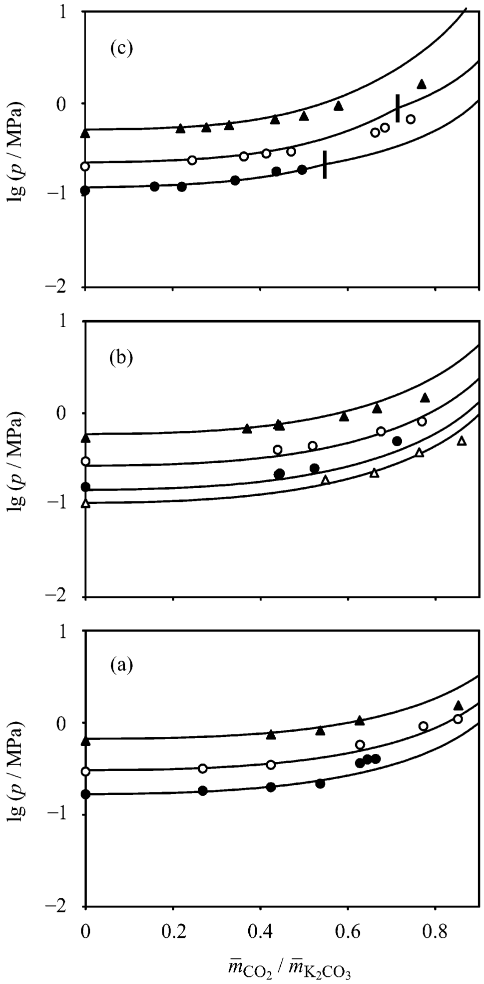

Figure 13. Total pressure above aqueous solutions of carbon dioxide and potassium carbonate at preset temperature and gas-free liquid-phase composition {(a) $\bar{w}_{K_2CO_3} = 0.3$ ($\bar{m}_{K_2CO_3} \approx 3.101$ mol·kg^{-1}), (b) $\bar{w}_{K_2CO_3} = 0.4$ ($\bar{m}_{K_2CO_3} \approx 4.824$ mol·kg^{-1}), (c) $\bar{w}_{K_2CO_3} = 0.5$ ($\bar{m}_{K_2CO_3} \approx 7.236$ mol·kg^{-1})}. Symbols = experimental data from Lyudkovskaya et al. [44] (△, $T = 383.15$ K; ●, $T = 393.15$ K; ○, $T = 413.15$ K; ▲, $T = 443.15$ K); —, prediction, this work. The vertical bars denote the limit from which—by addition of carbon dioxide—a deposition of potassium bicarbonate is predicted by the model.

Conclusions

In the present work, new experimental results for the solubility of carbon dioxide in aqueous solutions of either potassium chloride or potassium carbonate, covering wide ranges of conditions, are reported. The VLE of the systems (CO_2 + KCl + H_2O) and (CO_2 + K_2CO_3 + H_2O) (the latter allowing for the precipitation of $KHCO_3$) is described by means of a thermodynamic model based on Pitzer's molality scale based equation for the Gibbs excess energy of the aqueous phase. Model parameters are determined from the new carbon dioxide solubility data as well as from an extensive database adopted from the literature. The VLE (and VLSE) of the system (CO_2 + K_2CO_3 + H_2O) is particularly important in connection with the Hot Potassium Carbonate Process and its modifications by activating additives. These are commonly secondary and primary amines[7,8] (e.g., DEA[6] or piperazine),[9,10] which quickly and reversibly react with carbon dioxide, thereby accelerating the absorption rate of the gas.

To consistently describe the phase equilibrium for the solubility of carbon dioxide in aqueous solutions of potassium carbonate plus an additive one requires initially a reliable and extensive experimental data base and a sound correlation of the solubility of the sour gas in aqueous solutions of the single compounds potassium carbonate and the additive. In previous work,[34,56] a model for the VLE of the system (CO_2 + piperazine + H_2O), covering a temperature range from (313 to 393) K and stoichiometric piperazine molalities up to 4 mol·kg^{-1} was presented. That model may now be combined straightforwardly with the VLE (and VLSE) model for the system (CO_2 + K_2CO_3 + H_2O) developed in the present work, allowing for predictions of the VLE (and VLSE) of the overall system (CO_2 + K_2CO_3 + piperazine + H_2O).

Appendix 1

The stoichiometric molalities $\bar{m}_{K_2CO_3}$ and $\bar{m}_{CO_2}$ (covering regions II and III) are calculated from $\bar{m}^*_{KOH}$ and $\bar{m}^*_{CO_2}$ by

$$\bar{m}_{K_2CO_3} = \frac{\frac{1}{2}\bar{m}^*_{KOH}}{1 + \frac{1}{2}\frac{\bar{m}^*_{KOH}}{m^\circ}M^*_W} \tag{A1}$$

$$\bar{m}_{CO_2} = \frac{\bar{m}^*_{CO_2} - \frac{1}{2}\bar{m}^*_{KOH}}{1 + \frac{1}{2}\frac{\bar{m}^*_{KOH}}{m^\circ}M^*_W} \tag{A2}$$

where M^*_W is the relative molar mass of water divided by 1000 ($M^*_W = 0.01801528$), and $m^\circ = 1\ \mathrm{mol{\cdot}kg^{-1}}$. If, for example, $\bar{m}^*_{KOH} = 4\ \mathrm{mol{\cdot}kg^{-1}}$, then $\bar{m}_{K_2CO_3} \approx 1.9304\ \mathrm{mol{\cdot}kg^{-1}}$ (see Figure 1). Furthermore, in regions II and III, the following equation holds:

$$\frac{m_i}{\bar{m}_{K_2CO_3}} = \frac{m_i^*}{\frac{1}{2}\bar{m}^*_{KOH}} \tag{A3}$$

where m_i denotes the "true" molality of all solute species present in regions II and III (see also Figure 1).

It might be worth making two particular points in relation to Figure 1: At $\bar{m}_{CO_2}/\bar{m}_{K_2CO_3} = 0$, the stoichiometric composition of the liquid mixture can of course be expressed by the stoichiometric molality of K_2CO_3 alone, and at $\bar{m}_{CO_2}/\bar{m}_{K_2CO_3} = 1$, it can be expressed by the stoichiometric molality of $KHCO_3$ alone (cf., chemical reaction II). Therefore, the whole range of compositions within region II may also be expressed by the stoichiometric molalities of (K_2CO_3 and $KHCO_3$) alone ($\bar{m}^{**}_{K_2CO_3}$ and $\bar{m}^{**}_{KHCO_3}$, respectively). The equations to convert $\bar{m}_{K_2CO_3}$ and $\bar{m}_{CO_2}$ (covering only region II) to $\bar{m}^{**}_{K_2CO_3}$ and $\bar{m}^{**}_{KHCO_3}$ are

$$\bar{m}^{**}_{K_2CO_3} = \frac{\bar{m}_{K_2CO_3} - \bar{m}_{CO_2}}{1 - \frac{\bar{m}_{CO_2}}{m^\circ}M^*_W} \tag{A4}$$

$$\bar{m}^{**}_{KHCO_3} = \frac{2\,\bar{m}_{CO_2}}{1 - \frac{\bar{m}_{CO_2}}{m^\circ}M^*_W} \tag{A5}$$

Finally, within region III the composition of the liquid mixture may also be expressed by the stoichiometric molalities of ($KHCO_3$ and CO_2) alone ($\bar{m}^{***}_{KHCO_3}$ and $\bar{m}^{***}_{CO_2}$, respectively). The equations to convert $\bar{m}_{K_2CO_3}$ and $\bar{m}_{CO_2}$ (covering only region III) to $\bar{m}^{***}_{KHCO_3}$ and $\bar{m}^{***}_{CO_2}$ are

$$\bar{m}^{***}_{KHCO_3} = \frac{2\,\bar{m}_{K_2CO_3}}{1 - \frac{\bar{m}_{K_2CO_3}}{m^\circ}M^*_W} \tag{A6}$$

$$\bar{m}^{***}_{CO_2} = \frac{\bar{m}_{CO_2} - \bar{m}_{K_2CO_3}}{1 - \frac{\bar{m}_{K_2CO_3}}{m^\circ}M^*_W} \tag{A7}$$

Appendix 2

Pitzer's Molality Scale-Based Equation for the Excess Gibbs Energy. Pitzer's molality scale based equation for the excess Gibbs energy (G^E) of aqueous electrolyte solutions is[22,23]

$$\frac{G^E}{M^*_W n_W RT} = f(I) + \sum_{i,j \neq W}\sum \frac{m_i}{m^\circ}\frac{m_j}{m^\circ}\lambda_{ij}(I) + \sum_{i,j,k \neq W}\sum\sum \frac{m_i}{m^\circ}\frac{m_j}{m^\circ}\frac{m_k}{m^\circ}\mu_{ijk} \tag{A8}$$

The dielectric constant as well as the density of pure liquid water are required for the calculation of Pitzer's modification of the Debye−Hückel term $f(I)$. They were approximated from the properties of pure, saturated liquid water.[26,57] As usual, binary and ternary osmotic virial coefficients in Pitzer's G^E equation were treated as symmetric:

$$\lambda_{ij} = \lambda_{ji} \tag{A9}$$

$$\mu_{ijk} = \mu_{ikj} = \mu_{jik} = \mu_{jki} = \mu_{kij} = \mu_{kji} \tag{A10}$$

According to Pitzer's equations, λ_{ij} is written as:

$$\lambda_{ij} = \beta^{(0)}_{ij} + \beta^{(1)}_{ij}\, g(\alpha^{(1)}_{ij}\sqrt{I}) + \beta^{(2)}_{ij}\, g(\alpha^{(2)}_{ij}\sqrt{I}) \tag{A11}$$

where the ionic strength of the solution is given by

$$I = \frac{1}{2}\sum_i \frac{m_i}{m^\circ}z_i^2 \tag{A12}$$

and where z_i is the number of charges on solute i. $g(x)$ is defined as

$$g(x) = \frac{2}{x^2}[1 - (1 + x)\exp(-x)] \tag{A13}$$

$\beta^{(0)}_{ij}$, $\beta^{(1)}_{ij}$, $\beta^{(2)}_{ij}$, $\alpha^{(1)}_{ij}$, and $\alpha^{(2)}_{ij}$ are binary parameters. In the present work, $\alpha^{(1)}_{ij}$ is set to 2. Furthermore, $\beta^{(2)}_{ij}$ is set to 0; therefore, $\alpha^{(2)}_{ij}$ is not required. "Symmetrical and unsymmetrical mixing terms"[23] as well as all parameters describing interactions between ionic species carrying charges of the same sign were neglected.

When a single (chemically non-reacting) gas G is dissolved in pure water, the model contains only two interaction parameters ($\beta^{(0)}_{G,G}$ and $\mu_{G,G,G}$).

For binary systems (water + strong electrolyte $M_{\nu_+}X_{\nu_-}$) it is not possible to separate the influence of $\mu_{M,M,X}$ from that of $\mu_{M,X,X}$. Both ternary parameters are usually summarized in C^ϕ_{MX}:

$$C^\phi_{MX} = \frac{3}{\sqrt{\nu_+\nu_-}}[\nu_+\mu_{M,M,X} + \nu_-\mu_{M,X,X}] \tag{A14}$$

It is common practice to set either $\mu_{M,M,X}$ or $\mu_{M,X,X}$ to zero and to report $\beta^{(0)}_{M,X}$, $\beta^{(1)}_{M,X}$, and C^ϕ_{MX} (or $\mu_{M,X,X}$ or $\mu_{M,M,X}$).

In ternary systems (water + strong electrolyte $M_{\nu_+}X_{\nu_-}$ + gas G) it is similarly not possible to separate the influence of M and X on solute G. Therefore, it is common practice to use the following comprehensive parameters:

$$B^{(j)}_{G,MX} = \nu_+{\cdot}\beta^{(j)}_{G,M} + \nu_-{\cdot}\beta^{(j)}_{G,X}, \quad (j = 0, 1) \tag{A15}$$

$$\Gamma_{G,MX,MX} = \nu_+^2{\cdot}\mu_{G,M,M} + 2{\cdot}\nu_+{\cdot}\nu_-{\cdot}\mu_{G,M,X} + \nu_-^2{\cdot}\mu_{G,X,X} \tag{A16}$$

$$\Gamma_{G,G,MX} = \nu_+{\cdot}\mu_{G,G,M} + \nu_-{\cdot}\mu_{G,G,X} \tag{A17}$$

$B^{(1)}_{G,MX}$ is rarely needed to describe the solubility of a gas in an aqueous solution of a strong electrolyte. $B^{(0)}_{G,MX}$, $\Gamma_{G,MX,MX}$, and

$\Gamma_{G,G,MX}$ are usually sufficient for a good description of gas solubility. In $B^{(0)}_{G,MX}$, either $\beta^{(0)}_{G,M}$ or $\beta^{(0)}_{G,X}$ may be arbitrarily set to zero; in $\Gamma_{G,MX,MX}$, one can arbitrarily set two of the three parameters $\mu_{G,M,M}$, $\mu_{G,M,X}$, and $\mu_{G,X,X}$ to zero; and in $\Gamma_{G,G,MX}$, one can arbitrarily set either $\mu_{G,G,M}$ or $\mu_{G,G,X}$ to zero.

Appendix 3

Interaction Parameters in Pitzer's Equation for the Gibbs Excess Energy.

$$\beta^{(0)}_{K^+,Cl^-} = 0.04808 - 758.48\cdot\left[\frac{1}{(T/K)} - \frac{1}{298.15}\right] - 4.7062\cdot\ln\left[\frac{(T/K)}{298.15}\right] + 0.010072\cdot[(T/K) - 298.15] - 3.7599\times10^{-6}\cdot[(T/K)^2 - 298.15^2] \tag{A18}$$

$$\beta^{(1)}_{K^+,Cl^-} = 0.0476 + 303.9\cdot\left[\frac{1}{(T/K)} - \frac{1}{298.15}\right] + 1.066\cdot\ln\left[\frac{(T/K)}{298.15}\right] + 0.0470\cdot\ln[(T/K) - 260] \tag{A19}$$

$$\mu_{K^+,K^+,Cl^-} = \frac{1}{3}\left\{-7.88\times10^{-4} + 91.270\cdot\left[\frac{1}{(T/K)} - \frac{1}{298.15}\right] + 0.58643\ln\left[\frac{(T/K)}{298.15}\right] - 0.0012980\cdot[(T/K) - 298.15] + 4.9567\times10^{-7}\cdot[(T/K)^2 - 298.15^2]\right\} \tag{A20}$$

$$\beta^{(0)}_{CO_2,K^+} = 0.49547 - \frac{292.86}{(T/K)} + \frac{49047.9}{(T/K)^2} \tag{A21}$$

$$\mu_{CO_2,K^+,Cl^-} = -0.000989 \tag{A22}$$

$$\mu_{CO_2,CO_2,K^+} = -0.039588 + \frac{12.008}{(T/K)} \tag{A23}$$

$$\beta^{(0)}_{K^+,OH^-} = 0.1298 \tag{A24}$$

$$\beta^{(1)}_{K^+,OH^-} = 0.320 \tag{A25}$$

$$\mu_{K^+,K^+,OH^-} = \frac{0.0041}{3} \tag{A26}$$

$$\beta^{(0)}_{K^+,CO_3^{2-}} = 0.38621 - \frac{82.857}{(T/K)} \tag{A27}$$

$$\beta^{(1)}_{K^+,CO_3^{2-}} = 21.975 - \frac{6974.6}{(T/K)} \tag{A28}$$

$$\mu_{K^+,K^+,CO_3^{2-}} = -0.00872 + \frac{2.69}{(T/K)} \tag{A29}$$

$$\beta^{(0)}_{K^+,HCO_3^-} = 0.10662 - \frac{40.439}{(T/K)} \tag{A30}$$

$$\beta^{(1)}_{K^+,HCO_3^-} = 8.19 - \frac{2648}{(T/K)} \tag{A31}$$

$$\mu_{K^+,K^+,HCO_3^-} = -0.000348 + \frac{0.215}{(T/K)} \tag{A32}$$

$$\mu_{K^+,CO_3^{2-},HCO_3^-} = -0.0000118 - \frac{0.2181}{(T/K)} \tag{A33}$$

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