

2-naphthol, 135-19-3; carbon dioxide, 124-38-9; methanol, 67-56-1.

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COMMUNICATIONS

Correlation of Vapor-Liquid Equilibria for the System Ammonia-Carbon Dioxide-Water

New parameters are given for a previously published correlation for calculating vapor-liquid equilibria in aqueous systems containing volatile weak electrolytes. Particular attention is given to ternary aqueous mixtures containing ammonia and carbon dioxide. When the new parameters are used, good agreement is obtained with recent experimental data.

Aqueous waste streams from petroleum or petrochemical plants often contain volatile weak electrolytes such as ammonia, carbon dioxide, sulfur dioxide, hydrogen sulfide, and hydrogen cyanide. To prevent environmental pollution, these solutes must be removed, usually by distillation. For design of a separation operation, vapor-liquid equilibria are required. Edwards et al. (1975, 1978) have presented a correlation for calculating such equilibria as given in computer program TIDES (Pawlikowski et al., 1982a,b). (Some entries in Table VI of the 1982a paper are in error. The expressions listed for β_{ij}^0 with $i = \text{NH}_4^+$ and $j = \text{HCO}_3^-$, CO_3^{2-} , and CO_2 are actually those for $j = \text{CO}_2$, HCO_3^- , and CO_3^{2-} , in that order. For β_{ij}^0 with $i = \text{NH}_4^+$, the entries for $j = \text{OH}^-$ and NH_2COO^- should be switched.)

This work reports updated values for some dissociation equilibrium constants and Henry's constants. Particular attention is given to the ternary system ammonia-carbon dioxide-water; equilibria for that system are calculated at 100-205 °C and total liquid-phase concentrations to 10 *m*. Calculated results show good agreement with recent experimental data.

Dissociation Equilibrium Constants

In water, weak electrolytes dissociate partly into ions. Dissociation equilibrium constants are expressed as a function of temperature by

$$\ln K = A_1/T + A_2 \ln T + A_3T + A_4 \quad (1)$$

Table I gives coefficients A_1 - A_4 for nine reactions. For ammonia, carbon dioxide, hydrogen carbonate ion, hydrogen sulfide, hydrogen sulfide ion, sulfur dioxide, hydrogen sulfite ion, and hydrogen cyanide, the coefficients were determined from thermodynamic data given by Brewer (1982, 1986). For the carbamate reaction, the coefficients are based on equilibrium-constant data recommended by Mason (1982). These equilibrium constants are shown in Figure 1 with extrapolations to 300 °C.

Henry's Constants

Henry's constants were obtained as described by Edwards et al. (1978) using literature data for ammonia (Gillespie et al., 1985; Müller, 1983) and for carbon dioxide (Müller, 1983; Houghton et al., 1957). The effect of temperature is given by

$$\ln H = B_1/T + B_2 \ln T + B_3T + B_4 \quad (2)$$

Coefficients for ammonia and carbon dioxide are given in Table II. Figure 2 shows Henry's constants for ammonia and carbon dioxide for the temperature range 0-300 °C.

Molecule-Molecule Interaction Parameter

For concentrated solutions, liquid-phase interaction parameters are required for characterizing interactions between solute species (molecules and ions) in water. These parameters are not easily obtained, but fortunately they are much less important than equilibrium constants and Henry's constants.

Table I. Equilibrium Constants as a Function of Temperature (Equation 1)^a

	A_1	A_2	A_3	A_4	lowest-highest temp, °C (approx)
$\text{NH}_3 + \text{H}_2\text{O} = \text{NH}_4^+ + \text{OH}^-$	-5914.082	-15.06399	-0.01100801	97.97152	0-175
$\text{CO}_2 + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+$	-7726.010	-14.50613	-0.02798420	102.2755	0-225
$\text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+$	-9137.258	-18.11192	-0.02245619	116.7371	0-225
$\text{H}_2\text{S} = \text{HS}^- + \text{H}^+$	-18034.72	-78.07186	0.09198240	461.7162	0-275
$\text{HS}^- = \text{S}^{2-} + \text{H}^+$	-406.0035	33.88898	-0.05411082	-214.5592	0-225
$\text{SO}_2 + \text{H}_2\text{O} = \text{HSO}_3^- + \text{H}^+$	26404.29	160.3981	-0.2752224	-924.6255	0-175
$\text{HSO}_3^- = \text{SO}_3^{2-} + \text{H}^+$	-5421.930	-4.689868	-0.04987690	43.13158	0-175
$\text{HCN} = \text{CN}^- + \text{H}^+$	1182.631	44.46562	-0.0778234	-255.3364	0-175
$\text{NH}_3 + \text{HCO}_3^- = \text{NH}_2\text{COO}^- + \text{H}_2\text{O}$	604.1164	-4.017263	0.005030950	20.15214	0-160

^a Activities of all species (except water) are expressed by molality (mol/kg of H_2O). The activity of water is expressed by mole fraction. In practice, therefore, all equilibrium constants (except for the last reaction) have units of mol/kg. The last one has units of kg/mol.

Table II. Henry's Constants for NH_3 and CO_2 as a Function of Temperature (Equation 2)^a

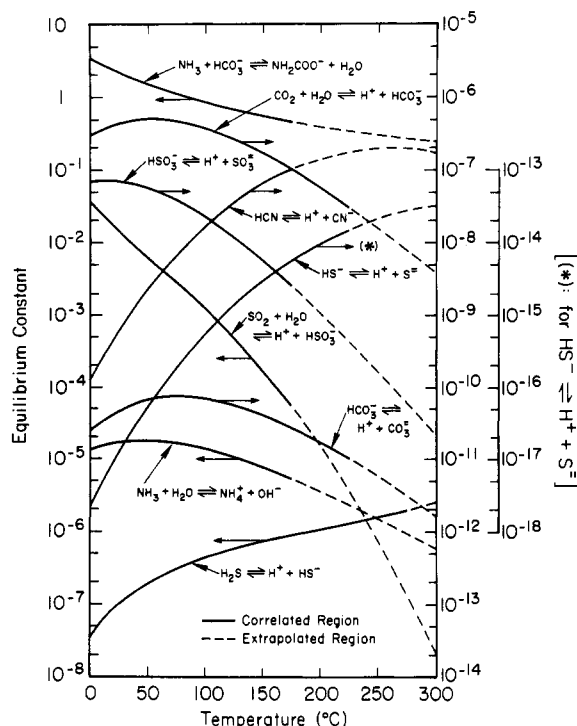
	B_1	B_2	B_3	B_4	lowest-highest temp, °C (approx)
NH_3	-7579.948	-13.58857	0.008596972	96.23184	0-300
CO_2	-17060.71	-68.31596	0.06598907	430.1920	0-200

^a H in bar·kg/mol.

Table III. Molecule-Molecule Interaction Parameter for NH_3 and CO_2 as a Function of Temperature (Equation 3)^a

	E	F	lowest-highest temp, °C (approx)
NH_3	-0.0398	17.0	0-300
CO_2	-0.0901	25.4	0-200

^a β in kg/mol.

**Figure 1. Equilibrium constants for some ionic reactions in water.**

Following the procedure described by Edwards et al. (1978), molecule-molecule interaction parameters are also obtained from data reduction for ammonia and for carbon dioxide. Figure 3 shows molecule-molecule interaction parameters for ammonia and for carbon dioxide; the data scatter badly, but they are fit reasonably well by the relation

$$\beta = E + F/T \quad (3)$$

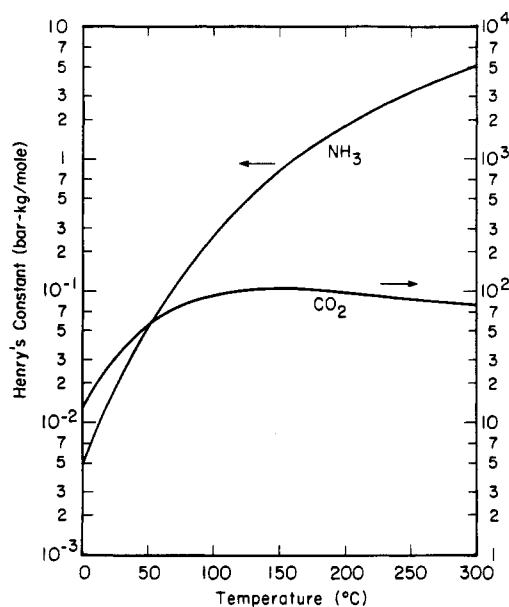
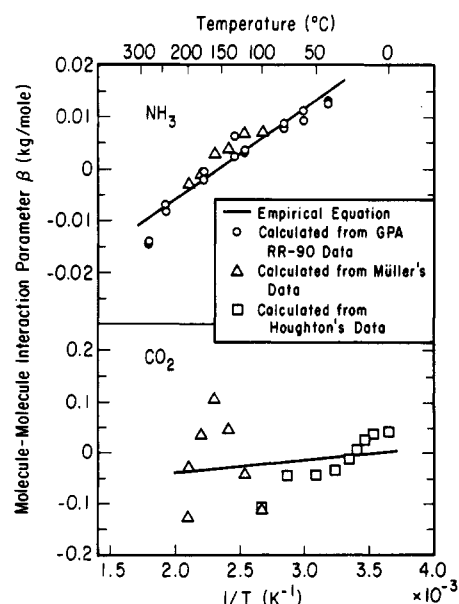
**Figure 2. Henry's constants for ammonia and for carbon dioxide.****Figure 3. Parameter β for ammonia and for carbon dioxide.**

Table IV. Experimental and Predicted Results for NH₃-CO₂-H₂O System at Two Temperatures

temp, °C	solute	total molality in liq	total and partial pressure, bar	
			exptl ^a	pred
148.89	NH ₃	1.15	0.412	0.359
	CO ₂	0.864	43.8	43.0
	total		50.0	48.9
204.59	NH ₃	1.41	2.84	2.36
	CO ₂	1.002	79.4	81.0
	total		107.6	106.4
148.89	NH ₃	2.31	1.73	1.51
	CO ₂	0.268	1.55	1.09
	total		8.27	7.08
204.59	NH ₃	2.354	4.68	4.13
	CO ₂	0.269	11.8	9.20
	total		34.8	30.4

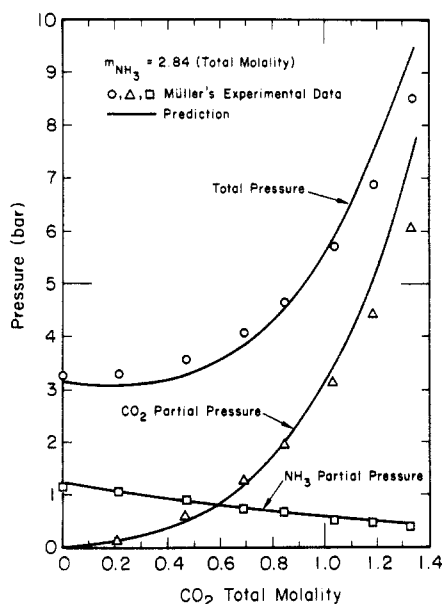
^a GPA RR-65 (Owens et al., 1983).Total and Partial Pressures in the System
NH₃-CO₂-H₂O at 120 °C**Figure 4.** Total and partial pressures in the system ammonia-carbon dioxide-water at 120 °C.

Table III gives the coefficients for eq 3. Figure 3 shows that both ammonia and carbon dioxide have very small molecule-molecule interaction parameters. Since the effect of these parameters is not significant for dilute or moderately dilute solutions, it may be best to set these parameters equal to zero.

Calculation of Ternary Vapor-Liquid Equilibria

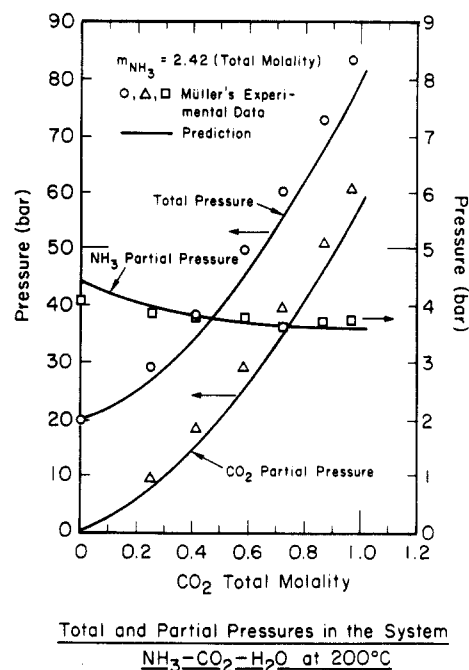
By use of the new dissociation equilibrium constants and Henry's constants, vapor-liquid equilibria were calculated for the ammonia-carbon dioxide-water system at 100–205 °C at various total concentrations to 10 *m*. The calculations were performed by using computer program TIDES which solves phase equilibria and dissociation equilibria simultaneously with mass balances and electroneutrality constraints. In these calculations, all liquid-phase interaction parameters (molecule-molecule, molecule-ion, ion-ion) are set equal to zero. Tables IV–VI and Figures 4 and 5 compare experimental and predicted vapor-liquid equilibria. In Table IV, experimental data are from Owens et al. (1983) at two temperatures. In Tables V and VI, experimental data are from Müller (1983) at 140 and 160

Table V. Experimental and Predicted Results for NH₃-CO₂-H₂O System at 140 °C

solute	total molality in liq	total and partial pressure, bar	
		exptl ^a	pred
NH ₃	4.003	2.44	2.40
CO ₂	0.233	0.330	0.196
total		6.47	5.99
NH ₃	4.012	1.92	1.80
CO ₂	0.815	2.94	2.43
total		8.68	7.66
NH ₃	4.015	1.50	1.45
CO ₂	1.221	7.00	6.42
total		12.46	11.4
NH ₃	4.032	0.285	1.06
CO ₂	1.835	19.06	19.7
total		23.76	24.5

^a Müller, 1983.**Table VI. Experimental and Predicted Results for NH₃-CO₂-H₂O System at 160 °C**

solute	total molality in liq	total and partial pressure, bar	
		exptl ^a	pred
NH ₃	7.65	6.56	6.36
CO ₂	0.644	2.25	1.21
total		15.11	13.1
NH ₃	7.65	5.71	5.06
CO ₂	1.50	8.75	6.18
total		20.98	16.9
NH ₃	7.66	4.27	3.83
CO ₂	2.49	24.21	21.2
total		35.6	31.1
NH ₃	7.68	3.30	3.33
CO ₂	3.07	40.12	38.5
total		51.5	48.3

^a Müller, 1983.Total and Partial Pressures in the System
NH₃-CO₂-H₂O at 200 °C**Figure 5.** Total and partial pressures in the system ammonia-carbon dioxide-water at 200 °C.

°C. In Figures 4 and 5, experimental data are also from Müller at 120 and 200 °C. Considering experimental uncertainties as well as limitations of the molecular-thermodynamic model in TIDES, experimental and predicted results show good agreement, appreciably better than that

obtained previously. Upon fitting the data of Owens et al., the new correlation gives errors about one-third those obtained when the earlier correlation is used. Upon fitting Müller's data, the new correlation gives errors about one-quarter those obtained when the earlier correlation is used.

The calculations reported here using the new parameters are based on all $\beta = 0$. When β for ammonia and for carbon dioxide are given by eq 3, and when all other β 's are from the previous correlation, the results are not changed very much except at high temperatures (160–200 °C) where the estimated total pressure is then excessively high, probably because the previous molecule-ion β parameters were erroneously extrapolated to high temperatures.

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Nomenclature

A_1 – A_4 = coefficients in eq 1
 B_1 – B_4 = coefficients in eq 2
 E , F = coefficients in eq 3
 H = Henry's constant, bar·kg/mol
 K = dissociation equilibrium constant
 T = temperature, K.

Greek Symbol

β = molecule–molecule interaction parameter

Registry No. NH_3 , 7664-41-7; CO_2 , 124-38-9.

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Selective Oxidative Coupling of Methane to Ethane and Ethylene over Supported Lead Oxide Catalysts

Catalytic performances of lead oxide supported on MgO which has been discovered to exhibit excellent characteristics for the oxidative coupling of methane to C_2 hydrocarbons have been studied. A 20 wt % PbO/MgO catalyst gave 13% methane conversion, 98% oxygen conversion, and 71% C_2 selectivity at 800 °C, a time factor of 1.0 g·h/mol, a feed gas composition for CH_4 of 14% and for O_2 of 1.6%, and atmospheric pressure. Significant changes of catalyst performance were observed with time. The methane conversion rate and C_2 selectivity as a function of PbO loading were examined to clarify that 5 wt % PbO loading was the best. It was also clarified that ethylene and carbon dioxide were made successively from ethane and carbon monoxide, respectively.

Methane is a main constituent of natural gas, of which proven reserves are very large. A large part of the current use of methane is restricted to fuel. In a chemical sense, methane has been used largely for the production of synthesis gas by steam reforming. Although the partial oxidation of methane to methanol or formaldehyde has been studied for many years, the selectivity level is not high enough for industrialization.

Recently, Keller and Bhasin (1982) have reported that ethane and ethylene were obtained by air oxidation of methane over several kinds of metal oxides supported on $\alpha\text{-Al}_2\text{O}_3$ at 500–1000 °C. Following that report, several investigators studied the same reaction with a variety of

metal oxide catalysts such as an alkalinized PbO/ $\gamma\text{-Al}_2\text{O}_3$ (Hinsen et al., 1984), a Li/MgO catalyst (Ito and Lunsford, 1985), rare earth metal oxides (Itsuka et al., 1985), and LaAlO_3 (Imai and Tagawa, 1986).

The present authors have examined the support effect of PbO catalysts to improve its activity and selectivity (Asami et al., 1986). As indicated in Figure 1, basic carriers such as MgO and $\beta''\text{-Al}_2\text{O}_3$ were found to give high yield and selectivity to C_2 hydrocarbons, while both the activity and selectivity for C_2 formation were very low over the catalysts supported on acidic carriers. Operating under optimum conditions, the selectivity to C_2 hydrocarbons reached 90% on the PbO/MgO catalyst. In the present