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R&D Note

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

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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; 1982a*,1982b).

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 to 205°C and total liquid-phase concentrations to 10 molal. 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

$$\ell nK = A_1/T + A_2 \ell nT + A_3 T + A_4 \qquad (1)$$

Table 1 gives coefficients A_1, A_2, A_3 and A_4 for nine reactions. For ammonia, carbon dioxide, hydrogen carbonate ion, hydrogen sulfide, hydrogen sulfide ion, sulfur dioxide, hydrogen sulfite ion, and

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* Some entries in Table VI of the 1982a paper are in error. The expressions listed for β^0_{ij} with $i=NH_4^+$ and $j=HCO_3^-$, CO_3^{2-}, and CO_2 are actually those for $j=CO_2$, HCO_3^-, and CO_3^{2-}, in that order. For β^1_{ij} with $i=NH_4^+$, the entries for $j=OH^-$ and NH_2COO^- should be switched.

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

$$\ell nH = B_1/T + B_2\ell nT + B_3T + B_4 \qquad (2)$$

Coefficients for ammonia and carbon dioxide are given in Table 2. Figure 2 shows Henry's constants for ammonia and carbon dioxide for the temperature range 0 to 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 K and Henry's constants H.

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

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

Table 3 gives the coefficients for Equation (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

Using the new dissociation equilibrium constants and Henry's constants, vapor-liquid equilibria were calculated for the ammonia-carbon dioxide-water system at 100 to 205°C at various total concentrations to 10 molal. The calculations were performed 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 4, 5 and 6 and Figures 4 and 5 compare experimental and predicted vapor-liquid equilibria. In Table 4, experimental data are from Owens et al. (1983) at two temperatures. In Tables 5 and 6, experimental data are from Müller (1983) at 140°C and 160°C. In Figures 4 and 5, experimental data are also from Müller at 120°C 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 Equation (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.

Acknowledgment

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Notation

A_1, A_2, A_3, A_4 = coefficients in Equation (1)

B_1, B_2, B_3, B_4 = coefficients in Equation (2)

E, F = coefficients in Equation (3)

H = Henry's constant, bar-kg/mole

K = dissociation equilibrium constant

T = temperature, K

Greek

β = molecule-molecule interaction parameter

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Table 1. Equilibrium Constants as a Function of Temperature

$$\ln K = A_1 / T + A_2 \ln T + A_3 T + A_4 \quad (T, K)$$

	A_1	A_2	A_3	A_4	Lowest-Highest Temperature(°C) (approximate)
$NH_3 + H_2O = NH_4^+ + OH^-$	-5914.082	-15.06399	-0.01100801	97.97152	0 - 175
$CO_2 + H_2O = HCO_3^- + H^+$	-7726.010	-14.50613	-0.02798420	102.2755	0 - 225
$HCO_3^- = CO_3^= + H^+$	-9137.258	-18.11192	-0.02245619	116.7371	0 - 225
$H_2S = HS^- + H^+$	-18034.72	-78.07186	0.09198240	461.7162	0 - 275
$HS^- = S^= + H^+$	-406.0035	33.88898	-0.05411082	-214.5592	0 - 225
$SO_2 + H_2O = HSO_3^- + H^+$	26404.29	160.3981	-0.2752224	-924.6255	0 - 175
$HSO_3^- = SO_3^= + H^+$	-5421.930	-4.689868	-0.04987690	43.31358	0 - 175
$HCN = CN^- + H^+$	1182.631	44.46562	-0.07782312	-255.3364	0 - 175
$NH_3 + HCO_3^- = NH_2COO^- + H_2O$	604.1164	-4.017263	0.005030950	20.15214	0 - 160

*) Activities of all species (except water) are expressed by molality (mol/kg-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 mole/kg. The last one has units of kg/mole.

Table 2. Henry's Constants for NH_3 and CO_2 as a Function of Temperature

$$\ln H = B_1 / T + B_2 \ln T + B_3 T + B_4 \quad (T, K)$$
$$(H, \text{bar-kg / mol})$$

	B_1	B_2	B_3	B_4	Lowest-Highest Temperature(°C) (approximate)
NH_3	-7579.948	-13.58857	0.008596972	96.23184	0 - 300
CO_2	-17060.71	-68.31596	0.06598907	430.1920	0 - 200

Table 3. Molecule-Molecule Interaction Parameter for NH_3 and CO_2 as a function of Temperature

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

$$(\beta, kg / mol)$$

	E	F	Lowest-Highest Temperature(°C) (approximate)
NH_3	-0.0398	17.0	0 - 300
CO_2	-0.0901	25.4	0 - 200

Table 4. Experimental and Predicted Results for NH_3-CO_2-H_2O System at two temperatures

Temperature (°C)	Solute	Total Molality in Liquid	Total & Partial Pressure(bar)	
			Experimental*	Predicted
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

* GPA RR-65(1983)

Table 5. Experimental and Predicted Results for NH_3-CO_2-H_2O System at 140°C

Solute	Total Molality in Liquid	Total & Partial Pressure(bar)	
		Experimental*	Predicted
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

* G. Müller(1983)

Table 6. Experimental and Predicted Results for NH_3-CO_2-H_2O System at 160°C

Solute	Total Molality in Liquid	Total & Partial Pressure(bar)	
		Experimental*	Predicted
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

* G. Müller(1983)

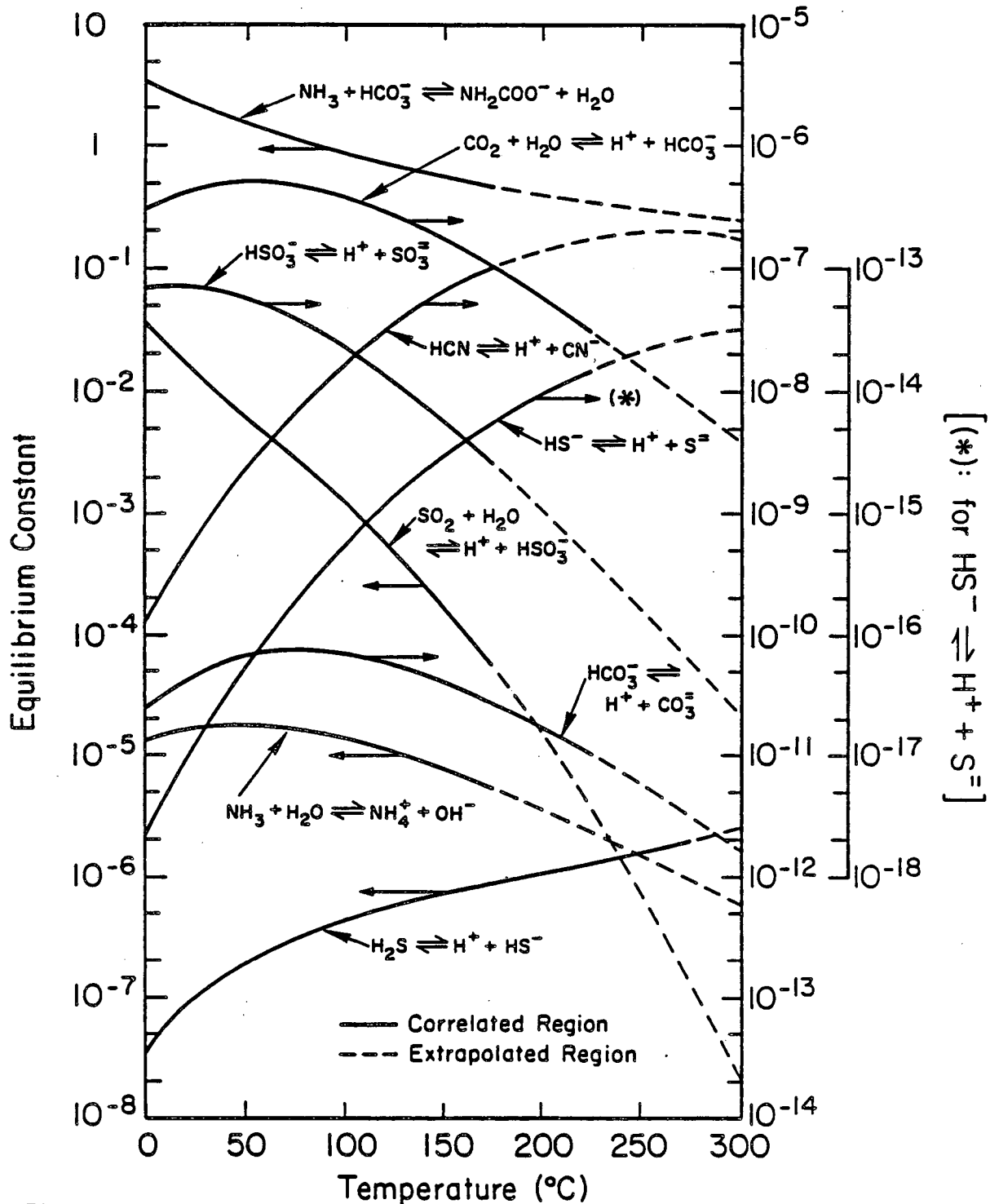

Figure 1

Equilibrium Constants for Some Ionic Reactions in Water

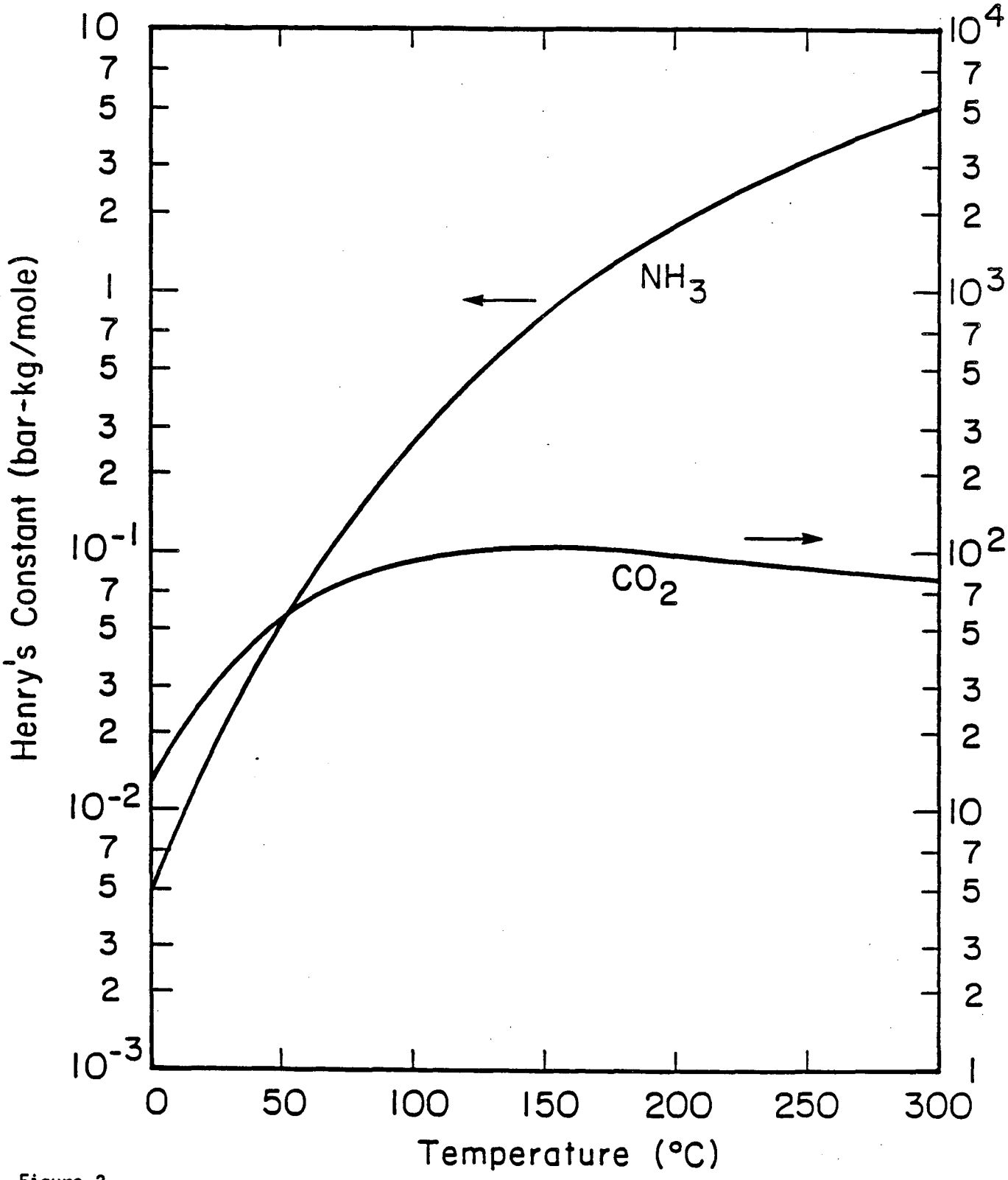

Figure 2

Henry's Constants for Ammonia and for Carbon Dioxide

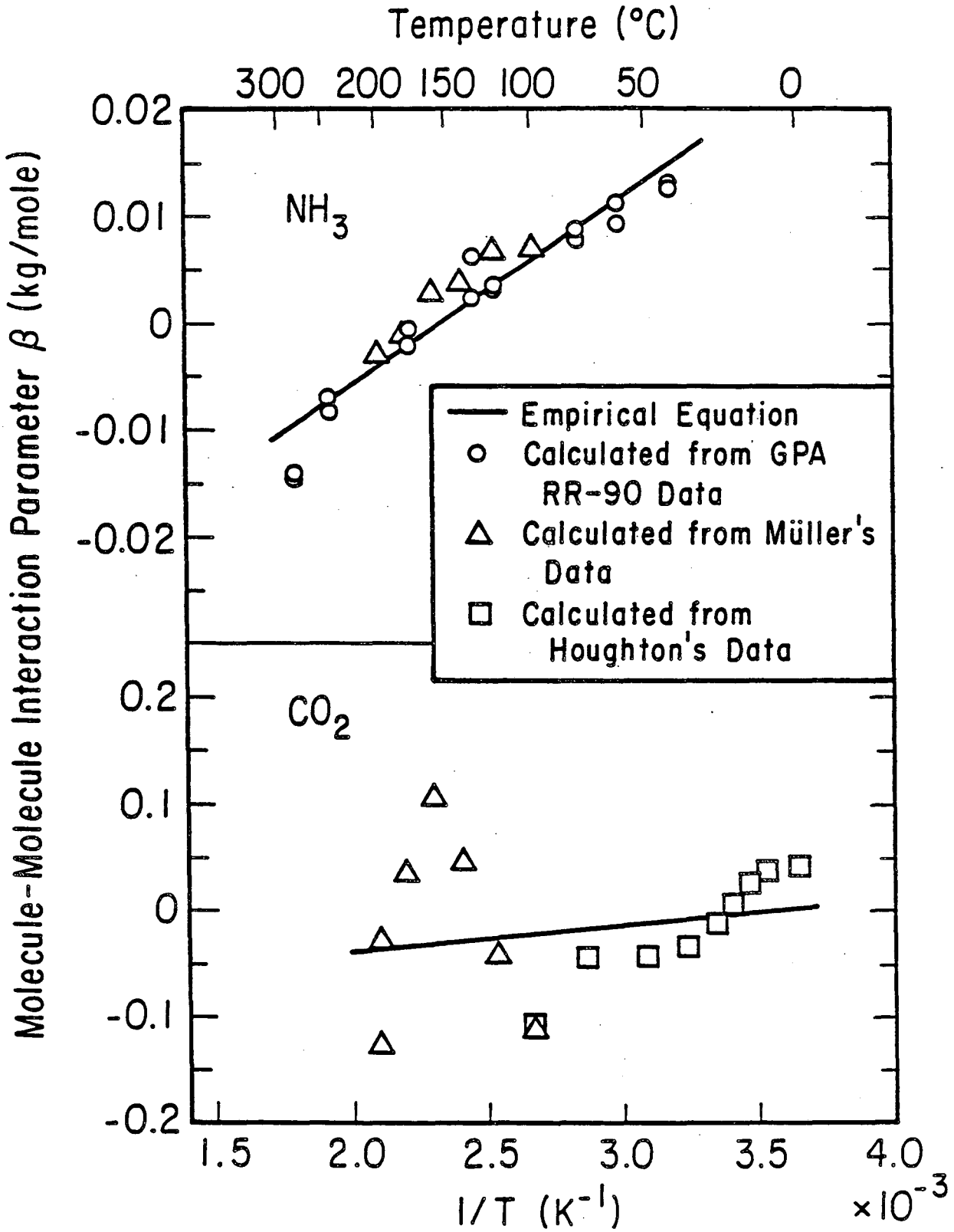

Figure 3

Parameter β for Ammonia and for Carbon Dioxide

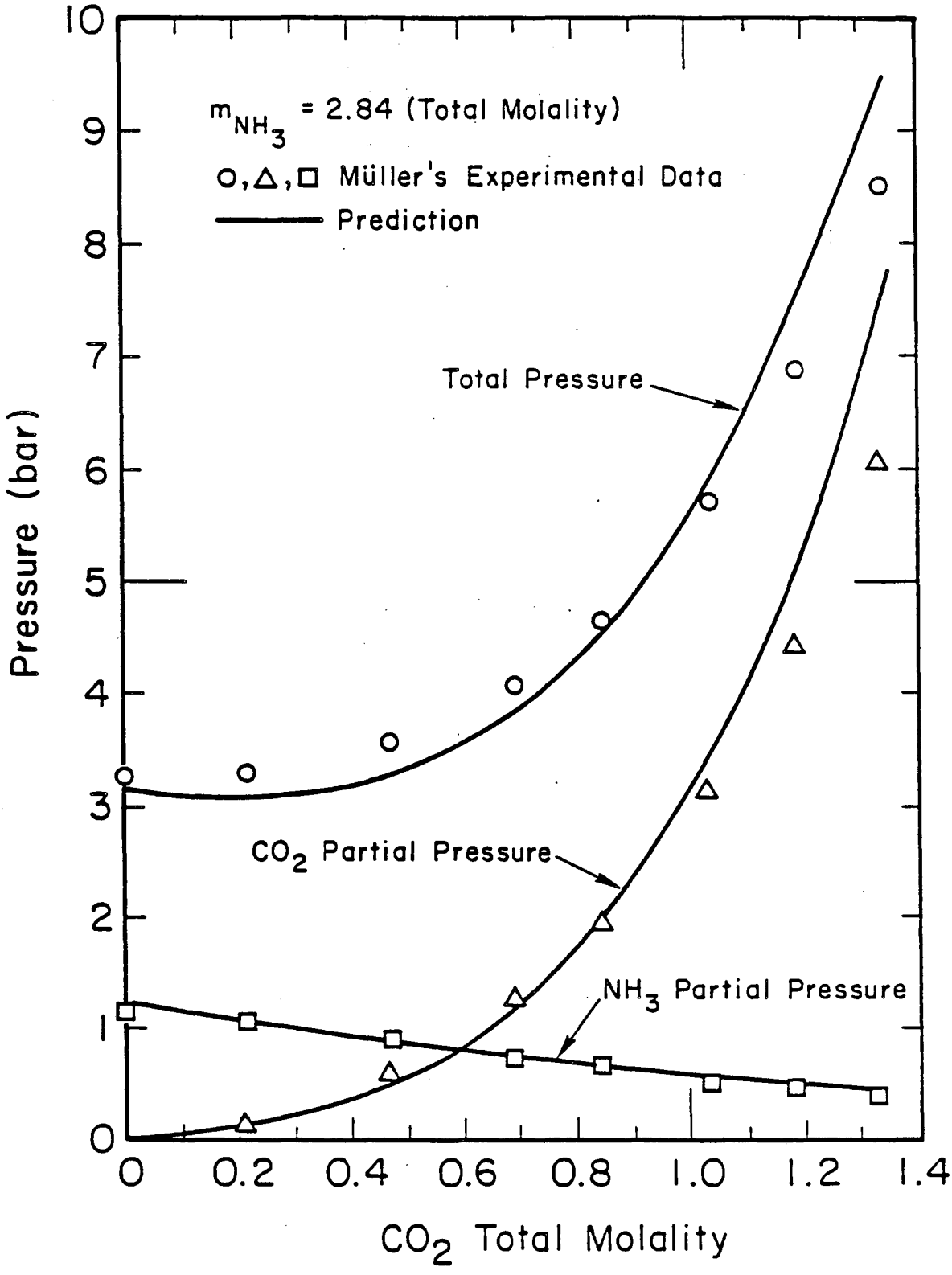

Figure 4

Total and Partial Pressures in the System $NH_3-CO_2-H_2O$ at 120°C

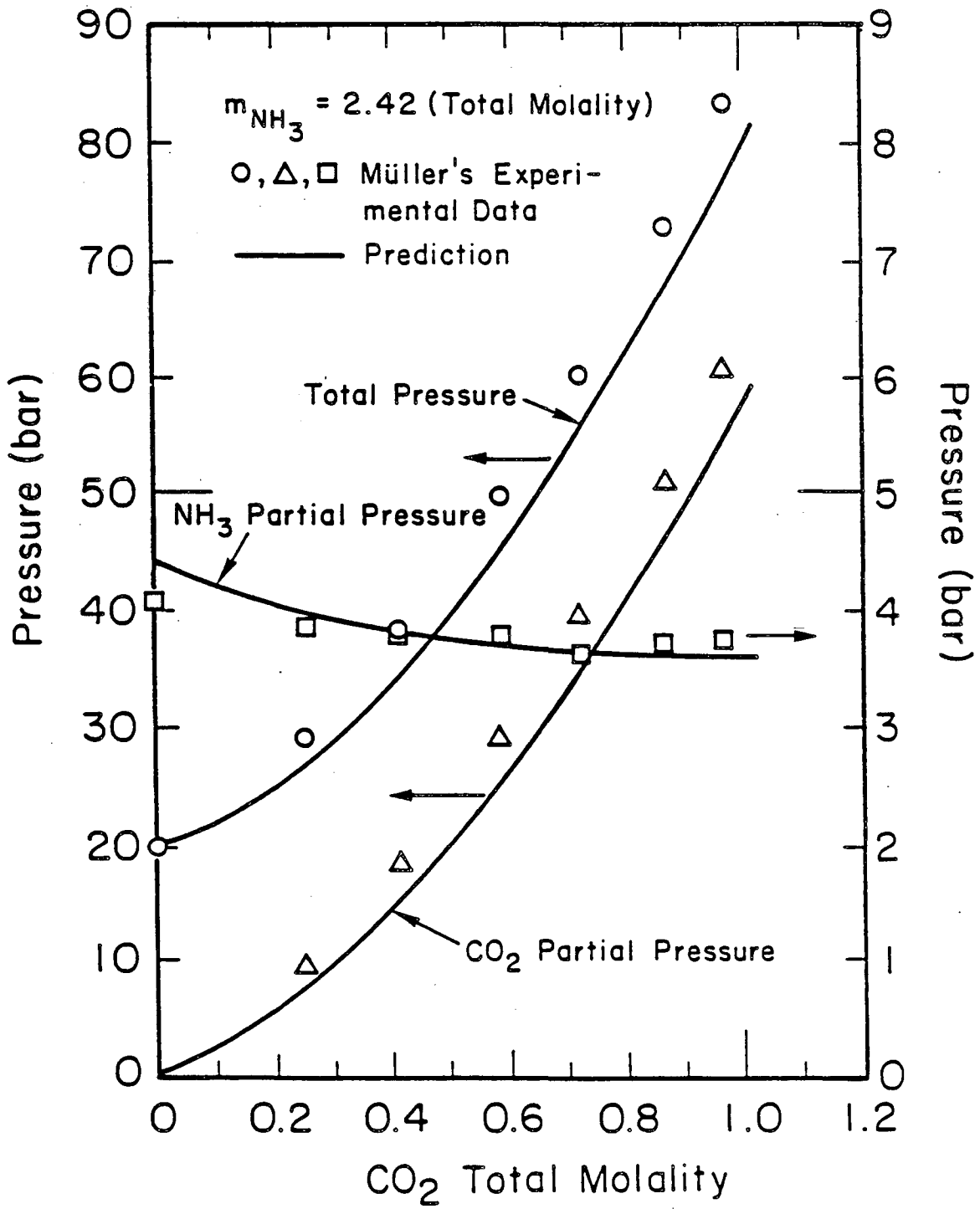

Figure 5

Total and Partial Pressures in the System $NH_3-CO_2-H_2O$ at 200°C

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