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Authors

Krei, G.A.

Harvey, A.H.

Prausnitz, J.M.

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G.A. Krei, A.H. Harvey, and J.M. Prausnitz

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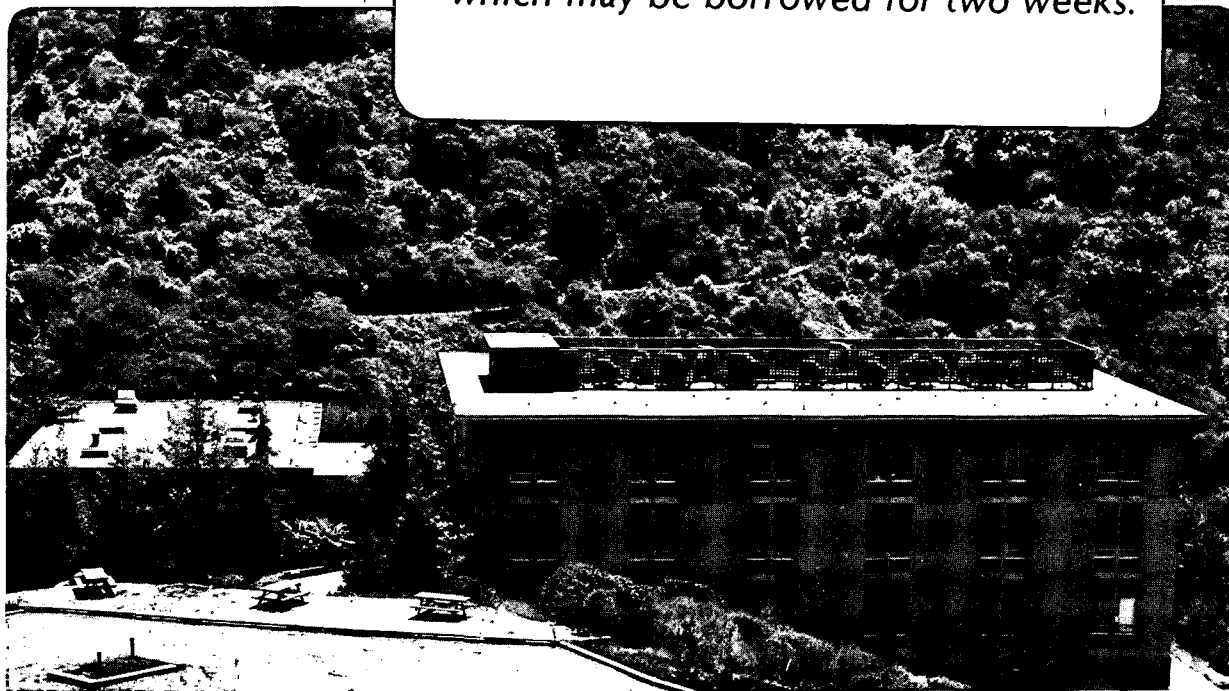
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Molecular Thermodynamics of Aqueous Solutions Containing Volatile Weak Electrolytes

Georg A. Krei
Allan H. Harvey
and
John M. Prausnitz

Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
and
Chemical Engineering Department
University of California
Berkeley, California 94720

ABSTRACT

A recent equation of state for aqueous mixtures containing electrolytes is extended to mixtures containing volatile weak electrolytes by superimposing chemical-dissociation equilibria in the liquid phase. To illustrate, calculated vapor-liquid equilibria are compared with experiment for the system water-carbon dioxide-ammonia in the region 100 - 200°C.

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Introduction

Increasing contamination of our environment makes us more aware of the importance of pollution control, e.g. waste-water treatment. In the chemical and petrochemical industry, effluent streams often contain volatile electrolytes (e.g. ammonia, carbon dioxide hydrogen sulfide and sulfur dioxide) which need to be removed efficiently. Towards that end, it is necessary to know the vapor-liquid equilibria of mixtures containing volatile electrolytes.

An extensive amount of work has been reported in the literature for aqueous mixtures containing strong electrolytes (Zemaitis et al. 1986), but there are few publications for systems containing weak electrolytes (van Krevelen 1949, Edwards et al. 1975, 1978, Jin and Donohue 1988). Most of these publications are based on activity-coefficient models which are not useful for concentrated multicomponent liquid mixtures containing supercritical gases (Prausnitz et al. 1986).

Recently, a new equation of state for mixtures containing electrolytes has been developed by Harvey and Prausnitz (1988). In a similar, earlier equation of state (Raatschen et al. 1987), ion-ion interactions are represented by Pitzer's virial expansion of the Debye-Hückel relation; in its more recent form, Pitzer's virial expansion is replaced by the Mean Spherical Approximation (Waisman and Lebowitz 1972, Blum 1980, Harvey et al. 1988). In this approximation, no ion-specific interaction parameters are needed; the only required parameters are the static dielectric constant of the fluid mixture and the size parameter σ_i of each ion. In practice, however, to obtain agreement with experiment, Harvey found that for each salt, one additional parameter must be known to account for hydration.

This work extends Harvey's equation of state to mixtures containing volatile weak electrolytes by superimposing chemical dissociation equilibria in the liquid phase. To illustrate, we calculate vapor-liquid equilibria for the ternary system water-carbon dioxide-ammonia (100 - 200 °C and pressures to 70 bar). Calculated results agree well with recent experiment (Müller et al. 1988).

Thermodynamic Framework

Figure 1 shows the essential physical situation in schematic form. Volatile weak electrolytes are distributed between the vapor and liquid phases. In the liquid phase, however, they exist in both molecular and ionic form. Since dissociation of electrolytes in the vapor phase is appreciable only at very high temperatures, it is neglected here.

For an aqueous mixture containing volatile weak electrolytes, our molecular-thermodynamic model determines phase equilibria, and chemical equilibria based on the following principles:

- At equilibrium, for every molecular (uncharged) component i ,

$$f_i^V = f_i^L \quad (1)$$

where f_i is the fugacity of component i at a fixed temperature and pressure. Superscript V refers to the vapor phase and superscript L refers to the liquid phase.

- A weak electrolyte in the liquid phase can exist in molecular or ionic form. The concentrations of these forms are determined from the total concentration through a material balance and a chemical equilibrium constant.

- Bulk electroneutrality in the liquid phase gives

$$0 = \sum_{i=1}^n x_i z_i \quad (2)$$

where x_i is the mole fraction and z_i is the charge of component i .

The chemical equilibrium constant K for each reaction is given by

$$K = \sum_{i=1}^m v_i a_i \quad (3)$$

where m is the number of reactants plus products of the reaction, v_i is a stoichiometric coefficient and a_i is the activity of component i . The activity a_i is related to fugacity by

$$a_i = \frac{f_i}{f_i^o} \quad (4)$$

where f_i^o is the fugacity of component i in a standard state. For solutes, we choose for the standard state a hypothetical ideal dilute solution at unit concentration at system temperature and standard

pressure (1 bar). For water, the (possibly hypothetical) standard state is pure liquid water at system temperature and standard pressure.

The chemical equilibrium constant can be estimated from thermodynamic data (Brewer 1982) through

$$-RT \ln K = \sum_{i=1}^m \nu_i G_i^o \quad (5)$$

where G_i^o is the Gibbs energy of formation of component i at system temperature T and in the standard state. The fugacity of component i in either phase can be expressed in terms of fugacity coefficients ϕ_i .

$$f_i^V = \phi_i^V y_i P \quad (6)$$

$$f_i^L = \phi_i^L x_i P \quad (7)$$

where y_i and x_i are mole fractions. Fugacity coefficients are obtained from Harvey's equation of state as summarized in the Appendix.

Determination of Parameters

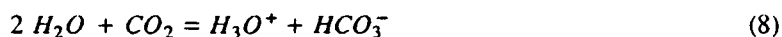
We apply our thermodynamic framework to calculate vapor-liquid equilibria for the system water-carbon dioxide-ammonia. In that system, the liquid-phase acid-base reaction of carbon dioxide with ammonia produces solubilities in water significantly higher than those for each solute alone. While dissociation is important in the ternary system, it is negligible in the binaries carbon dioxide-water and ammonia-water [except for extremely low solute concentrations (Edwards et al. 1978)]. We use Harvey's equation of state to describe the vapor-liquid equilibria of these binary systems. Table 2 gives the adjustable binary parameters k_{ij} obtained by fitting the equation of state to experimental binary data for carbon dioxide-water and ammonia-water (Rizvi and Heidemann 1987, Müller 1988).

Figures 2 and 3 show K-factors for the more volatile component in the binary systems at 160 °C. For carbon dioxide-water we find good agreement between calculated and experimental results. The average error is 5%. For the binary ammonia-water the equation of state tends to overpredict the relative volatility of ammonia. However, the bubble-point curve is matched much better than the

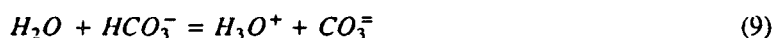
dew-point curve (the average errors are 5% and 13%, respectively), consistent with observations by Heidemann and Rizvi (1986) and Peng and Robinson (1980), who noted the difficulty of matching equilibrium vapor compositions in this system when using equation-of-state models.

In the ternary system, five dissociation equilibria must be taken into account:

-the formation of bicarbonate ion



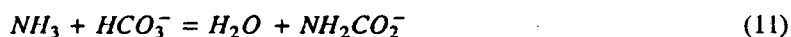
-the formation of carbonate ion



-the formation of ammonium ion



-the formation of carbamate ion



-and, very important, the dissociation of water



Chemical equilibria are determined by chemical dissociation equilibrium constants K . The temperature dependence of each chemical equilibrium constant is represented in the form

$$\ln K = A_1/T + A_2 \ln T + A_3 T + A_4 \quad (13)$$

Table 3 gives coefficients $A_1 - A_4$ for the five reactions of interest (Kawazuishi and Prausnitz 1987, Edwards et al. 1975).

Our thermodynamic framework describes the influence of electrostatic forces on the Helmholtz energy of a fluid mixture using the primitive model. We therefore require the static dielectric constant D of the fluid. For equation-of-state calculations, the dielectric constant is given as a function of temperature, density and composition, as shown by Harvey and Prausnitz (1987).

The effect of intermolecular forces on the Helmholtz energy of a fluid mixture is strongly dependent on the molecular size of each component. For molecular (uncharged) species, the molecular diameter σ_i is obtained by fitting the equation of state to pure-component vapor-pressure data. For ionic species it is common to use the diameter determined from crystallographic data (Pauling

1960, Jenkins 1979). However, since results are very sensitive to this parameter, we use instead an aqueous diameter (Marcus 1983). The aqueous diameter of a molecular ion is about 10% larger than the crystal diameter. For ions where aqueous diameters are not available, we increase the crystal diameter by 10%.

According to the primitive model adopted here, cations are centered in a cavity with diameter $\sigma_{i,cav}$ which is larger than ionic diameter σ_i . Cavity diameters $\sigma_{i,cav}$ are taken from Rashin and Honig (1985).

For ionic species, we require the static polarizability α_i (eqn. A-8). However, while many data have been reported for the static polarizability α_i of atomic ions, only few data are available for molecular ions (Benson 1976). For the estimation of the mean static polarizability of uncharged species we use group-contribution methods based on the additivity of bond polarizabilities (Landolt-Börnstein, Miller 1979). For molecular anions, where no data are available, we estimate the polarizability of the equivalent uncharged molecule (whose chemical structure is the same as that of the ion, except for the additional hydrogen atom). We then correct for "dehydrogenation". For anions where the charge is located at an oxygen atom, the correction is obtained by taking the difference between the static polarizability of water (1.59 \AA^3) and that of the hydroxyl ion (2.0 \AA^3).

Unfortunately, our calculated Helmholtz-energy model does not account for all effects known to exist in an electrolyte solution. Since the primitive model does not consider specific ion-solvent interactions, hydration effects must be included. Further, effects due to the polar nature of some ions have to be taken into account, since for ions only a temperature-independent Lennard-Jones parameter ϵ_i can be derived (eqn. A-8), while our thermodynamic model accounts for polar forces using a temperature-dependent attractive-energy parameter (eqn. A-7). We incorporate these effects into the attractive energy parameter ϵ_{ij} between ions and water (eqn. A-10). The binary parameter k_{ij} for this interaction is then adjusted to experimental vapor-liquid-equilibrium data.

For the system water-carbon dioxide-ammonia we fit only the binary parameters ammonium-water and bicarbonate-water, since these ions usually account for about 90% of the ionic strength of the liquid. All other ion-water parameters are set to zero. In principle, the binary parameters

ammonium-water and bicarbonate-water could be adjusted to binary data; however, since dissociation is negligible for the systems ammonia-water and carbon dioxide-water, we determine $k_{NH_4^+-H_2O}$ and $k_{HCO_3^--H_2O}$ using ternary data. For the temperature region 100 - 200 °C we obtain:

$$k_{NH_4^+-H_2O} = k_{HCO_3^--H_2O} = -0.4164 + 0.00125 T/[K] \quad (14)$$

where $k_{ion-water}$ equals $k_{water-ion}$. Fitting the binary parameters for the different ions individually does not bring any significant improvement.

Results and Discussion

Using our molecular-thermodynamic model and constants, vapor-liquid equilibria have been calculated at several temperatures for the system water-carbon dioxide-ammonia. Tables 5 and 6 and Figures 4 and 5 compare calculated and experimental results (Müller et al. 1988) showing fair agreement. Remaining discrepancies are partly due to the equation of state's inadequacy for representing vapor-liquid equilibria of the binary system ammonia-water. In addition, there is appreciable uncertainty in the carbamate equilibrium constant (Kawazuishi 1987) because only very few data are available for carbamate formation (Edwards 1978). However, a more significant source of error probably follows from our oversimplified representation of hydration effects in the equation of state, as given by an adjustable ion-water Lennard-Jones parameter.

Computation of vapor-liquid equilibria of mixtures containing weak electrolytes requires careful programming. While in systems containing strong electrolytes the concentration of ions is determined through mass balances only, we here have to respect chemical dissociation equilibria as well. This requires the computation of fugacity coefficients of ionic species, which may take on values significantly higher than those for nonionic components, as shown in Table 7. Therefore, caution is necessary to maintain computational accuracy.

For vapor-liquid equilibria of mixtures containing weak electrolytes activity coefficients provide a more useful measure than fugacity coefficients because activity coefficients are based on the infinite-dilution standard state at which the chemical equilibrium constant is defined. Further, this standard state is much closer to the state of interest than the ideal-gas standard state of the equation

of state. For any species i , the activity coefficient γ_i is given by:

$$\gamma_i = \frac{\phi_i P}{\phi_i^\circ P^\circ} \quad (15)$$

Figure 6 shows activity coefficients for all liquid-phase components in the system water-carbon dioxide-ammonia at 160 °C. All activity coefficients are within a reasonable range and show the expected tendency: for all components except water, they decrease with rising overall concentration of carbon dioxide. In this ammonia-rich solution, since almost all carbon dioxide in the liquid phase is present in ionic form, the overall mole fraction of carbon dioxide is essentially proportional to the ionic strength of the fluid.

Within our molecular-thermodynamic framework, the most important parameters are the size parameters σ_i of ionic species, since they affect all four contributions to the residual Helmholtz energy considered in this model. Therefore, choice of the ionic size parameters has major influence on calculated vapor-liquid equilibria. In general, increasing ionic diameters lower the activity coefficients of the ionic species, thereby raising the solubility of the solutes in the liquid phase and lowering their partial pressures. However, the size parameters of the hydronium and hydroxyl ions are only of minor importance.

Acknowledgments

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Additional support was provided in the form of a fellowship to G.A.K. from COMACO-Germany. The authors are grateful to Prof. L. Brewer for helpful discussions.

Appendix

Harvey's equation of state for aqueous mixtures containing electrolytes follows from a residual-Helmholtz-energy model which sums contributions from several molecular interactions:

$$A^r(T, \rho, \underline{x}) = \Delta A_I + \Delta A_{II} + \Delta A_{III} + \Delta A_{IV} \quad (\text{A-1})$$

The residual Helmholtz energy A^r is expressed as a function of temperature T , density ρ and composition \underline{x} . Fugacity coefficients are obtained from the partial composition derivatives:

$$\ln \phi_i = \left(\frac{\partial (A^r/RT)}{\partial n_i} \right)_{T, \rho, n_{j \neq i}} - \ln \left(\frac{PV}{nRT} \right) \quad (\text{A-2})$$

The total pressure is obtained upon differentiation with respect to density:

$$P = - \left(\frac{\partial A^r}{\partial V} \right)_{T, \underline{n}} + \frac{nRT}{V} \quad (\text{A-3})$$

The effect of nonionic forces (dispersion, dipole-dipole, etc.) within a fluid phase are described with a Lennard-Jones potential using Barker-Henderson perturbation theory. The Helmholtz energy of the reference mixture of hard spheres is given by the Boublik-Mansoori extension of the Carnahan-Starling equation

$$\Delta A_I = nRT \left(\frac{\frac{3DE}{F} \xi - \frac{E^3}{F^2}}{(1-\xi)} + \frac{\frac{E^3}{F^2}}{(1-\xi)^2} + \left(\frac{E^3}{F^2} - 1 \right) \ln(1-\xi) \right) \quad (\text{A-4})$$

$$D = \sum_{i=1}^n x_i \sigma_i; \quad E = \sum_{i=1}^n x_i \sigma_i^2; \quad F = \sum_{i=1}^n x_i \sigma_i^3$$

$$\xi = \frac{\pi}{6} \rho N_{Av} F; \quad \rho = n/V$$

Here, N_{Av} is Avogadro's number and V is the total volume. The perturbation term is a series expansion in reciprocal temperature truncated after the second term

$$\Delta A_{II} = nRT \left(\frac{a^{(1)}}{\tilde{T}} + \frac{a^{(2)}}{\tilde{T}^2} \right) \quad (\text{A-5})$$

where $a^{(1)}$ and $a^{(2)}$ are functions of the reduced molar density $\tilde{\rho}$. The reduced temperature \tilde{T} is defined by

$$\tilde{T} = kT/\varepsilon \quad (\text{A-6})$$

where k is Boltzmann's constant and ε is the Lennard-Jones attractive energy parameter. For (non-ionic) component i , the parameter ε_i is a function of temperature

$$\frac{\varepsilon_i}{k} = \frac{\varepsilon_i^{(0)}}{k} + \frac{\varepsilon_i^{(1)}}{k} \exp\left(\varepsilon_i^{(2)} \frac{T}{T_{ci}}\right) \quad (\text{A-7})$$

where T_{ci} is the critical temperature of component i and $\varepsilon_i^{(0)}$ - $\varepsilon_i^{(2)}$ are adjustable parameters.

The attractive Lennard-Jones parameter ε_i of ionic components can be determined using dispersion theory (Mavroyannis and Stephen 1962):

$$\frac{\varepsilon_i}{k} = 2.2789 \cdot 10^{-8} \alpha^{1.5} Z_i^{0.5} \sigma_i^{-6} \quad (\text{A-8})$$

where α_i is the static polarizability in cm^3 , Z_i is the number of electrons per ion and σ_i is the crystal diameter of ion i in cm.

For multi-component systems, the attractive-energy parameter ε of the mixture follows from van der Waals' one-fluid theory and is determined through a volume fraction mixing rule.

$$\varepsilon = \frac{\sum_{i=1}^n \sum_{j=1}^n x_i x_j \sigma_{ij}^3 \varepsilon_{ij}}{\sum_{i=1}^n x_i \sigma_i^3} \quad (\text{A-9})$$

where σ_{ij} is the arithmetic mean of the hard-sphere diameters of components i and j . The attractive energy parameter ε_{ij} for i - j interactions is given by a corrected geometric-mean combining rule:

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2} \left(1 - k_{ij} + (k_{ij} - k_{ji}) \frac{x_i}{x_i + x_j} \right) \quad (\text{A-10})$$

where k_{ij} and k_{ji} are adjustable binary parameters that may be temperature dependent:

$$k_{ij} = k_{ij}^{(0)} + k_{ij}^{(1)}/T \quad (\text{A-11})$$

For gas-water binaries, it is usually sufficient to make only $k_{\text{gas-water}}$ temperature-dependent.

The effect of ionic forces on the system is described using the so-called primitive model (Born 1920, Rashin and Honig 1985): a charged hard sphere is centered in a cavity (of diameter $\sigma_{i,\text{cav}}$) in a continuous medium with dielectric constant D . For cations, cavity diameter $\sigma_{i,\text{cav}}$ is larger than the

Lennard-Jones diameter σ_i of the ion, while for anions, the diameter of the cavity is equal to that of the ion (Rashin and Honig 1985). Using this model, the well-known Born term accounts for electrostatic interactions between ions and the bulk solvent phase, characterized by the dielectric constant D :

$$\Delta A_{III} = \frac{N_{Av} e^2}{RT} \sum_{i=1}^m x_i z_i^2 \left(\frac{1}{D\sigma_{i,cav}} + \frac{1}{\sigma_i} - \frac{1}{\sigma_{i,cav}} \right) \quad (A-12)$$

where e is the unit electronic charge. Ion-ion interactions are taken into account by the Mean Spherical Approximation (MSA) which is based on the primitive model (Waisman and Lebowitz 1972, Blum 1980, Harvey et al. 1988).

$$\Delta A_{IV} = - \frac{(2\Gamma)^3 (1 + 1.5\Gamma\bar{\sigma})}{12\pi N_{Av}\rho} \quad (A-13)$$

with the screening factor Γ given by

$$\Gamma = \frac{1}{2\bar{\sigma}} \left(\sqrt{1 + 2\bar{\sigma}\kappa} - 1 \right) \quad (A-14)$$

$$\kappa^2 = \frac{4\pi e^2 N_{Av}\rho}{DkT} \sum_{i=1} x_i z_i^2 \quad (A-15)$$

where the summation is over all ionic species. The mean ionic diameter $\bar{\sigma}$ is calculated by

$$\bar{\sigma} = \frac{\sum_{i=1} x_i \sigma_i}{\sum_{i=1} x_i} \quad (A-16)$$

where the summation is again over all ionic species.

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Table 1: Pure-Component Equation-of-State Parameters for H₂O, CO₂, and NH₃

	σ [Å]	$\epsilon^{(0)} / k$ [K]	$\epsilon^{(1)} / k$ [K]	$\epsilon^{(2)}$ [-]
H ₂ O	3.0049	100.0	597.76	0.31616
CO ₂	4.1254	150.0	177.28	0.93909
NH ₃	3.3123	227.05	191.17	0.63676

Table 2: Binary Parameters $k_{ij}^{(0)}$ [-] and $k_{ij}^{(1)}$ [K]

$i \backslash j$	H ₂ O	CO ₂	NH ₃
H ₂ O		0.02852 0.0	- 0.2298 0.0
CO ₂	- 0.1037 -66.11		
NH ₃	- 0.0821 -43.15		

Table 3: Chemical Equilibrium Constants as a Function of Temperature (Equation 13)

	A_1	A_2	A_3	A_4	temperature range, °C
$2\text{H}_2\text{O} + \text{CO}_2 = \text{H}_3\text{O}^+ + \text{HCO}_3^-$	- 7 726.010	- 14.506 13	- 0.027 984 20	102.275 5	0 - 225
$\text{H}_2\text{O} + \text{HCO}_3^- = \text{H}_3\text{O}^+ + \text{CO}_3^{2-}$	- 9 137.258	- 18.111 92	- 0.022 456 19	116.737 1	0 - 225
$\text{H}_2\text{O} + \text{NH}_3 = \text{NH}_4^+ + \text{OH}^-$	- 5 914.082	- 15.063 99	- 0.011 008 01	97.971 52	0 - 175
$\text{HCO}_3^- + \text{NH}_3 = \text{H}_3\text{O}^+ + \text{NH}_2\text{CO}_2^-$	640.1164	- 4.017 263	0.005 030 950	20.152 14	0 - 160
$2\text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OH}^-$	- 13 445.9	- 22.477 3	0.0	140.932	0 - 225

Table 4: Diameters, Static Polarizabilities, and Lennard-Jones Parameters for Ions

	σ_{cr} [Å]	σ_{aq} [Å]	σ_{cav} [Å]	α [Å ³]	ϵ/k [K]
H_3O^+		2.26 ^M	2.9	1.2 ^B	711.0
NH_4^+	2.96 ^P	3.32 ^M	4.26 ^R	1.6 ^B	108.9
OH^-	2.66 ^J	2.98		2.0 ^B	291.1
HCO_3^-	3.12 ^J	3.43		4.8	832.5
CO_3^{2-}	3.56 ^J	4.0		5.2	373.2
$NH_2CO_2^-$		3.9		5.4	459.7

B: Benson (1976); J: Jenkins (1979); M: Marcus (1983); P: Pauling (1960); R: Rashin (1985)

Table 5: Calculated and Experimental Total and Partial Pressures for Water-Carbon Dioxide-Ammonia at 120 °C

solute	overall mole fraction in liquid	total and partial pressures, bar	
		exptl ^M	calc
CO ₂	0.0287	0.63	0.81
NH ₃	0.1746	4.54	4.13
total		6.92	6.58
CO ₂	0.0430	1.43	1.63
NH ₃	0.1722	3.71	3.40
total		6.92	6.68
CO ₂	0.0527	2.41	2.43
NH ₃	0.1705	3.15	2.94
total		7.31	7.04
CO ₂	0.0660	5.03	4.09
NH ₃	0.1683	2.34	2.38
total		9.09	8.15

M = Müller 1988

Table 6: Calculated and Experimental Total and Partial Pressures for Water-Carbon Dioxide-Ammonia at 180 °C

solute	overall mole fraction in liquid	total and partial pressures, bar	
		exptl ^M	calc
CO ₂	0.0199	10.23	10.33
NH ₃	0.1819	16.62	15.71
total		37.80	34.98
CO ₂	0.0325	21.08	21.08
NH ₃	0.1795	15.40	14.69
total		47.60	44.95
CO ₂	0.0412	31.71	29.99
NH ₃	0.1778	15.00	14.08
total		57.60	53.48
CO ₂	0.0485	42.76	38.71
NH ₃	0.1761	15.60	13.58
total		69.60	61.82

M = Müller 1988

Table 7: Fugacity Coefficients ϕ_i°
for Water-Carbon Dioxide-Ammonia
at 160 °C and Standard State *

component	$\ln \phi_i^\circ$
H ₂ O	1.79
CO ₂	8.71
NH ₃	3.86
H ₃ O ⁺	46.8
NH ₄ ⁺	40.9
OH ⁻	9.72
HCO ₃ ⁻	3.21
CO ₃ ⁼	15.8
NH ₂ CO ₂ ⁻	6.5

* Standard State:

for solutes:

a hypothetical ideal solution at unit
concentration at temperature T and
P^o = 1 bar

for water:

pure liquid water at temperature T
and P^o = 1 bar

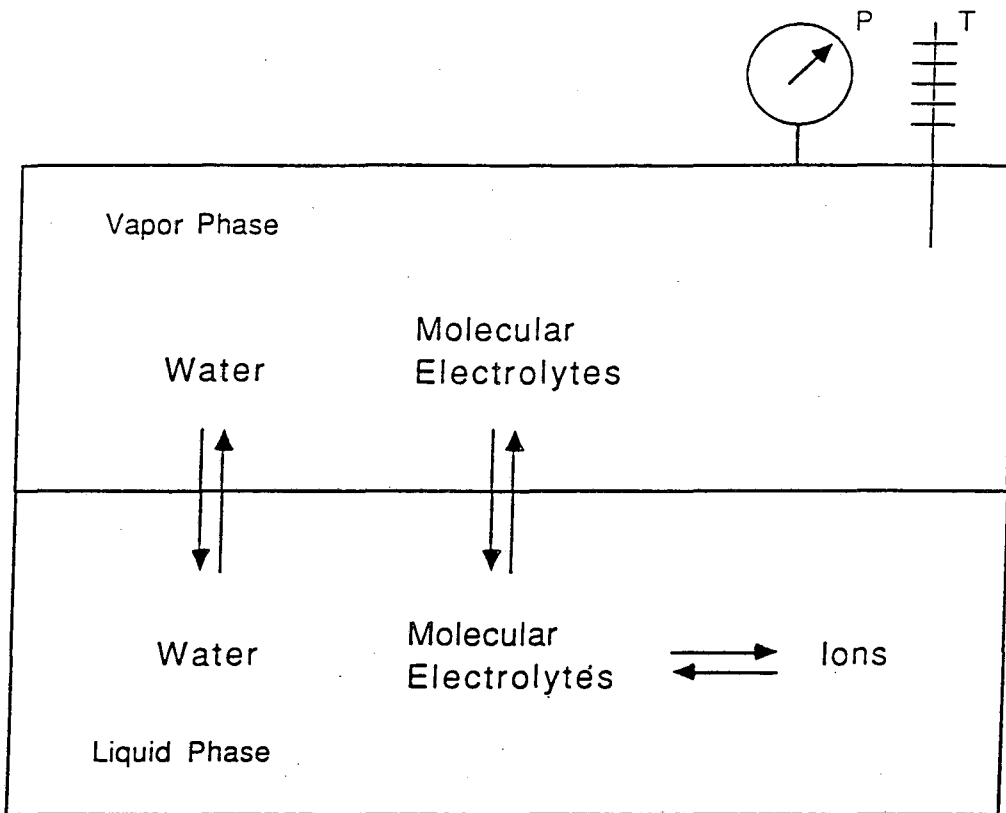


Figure 1: Equilibria in an aqueous system containing volatile weak electrolytes

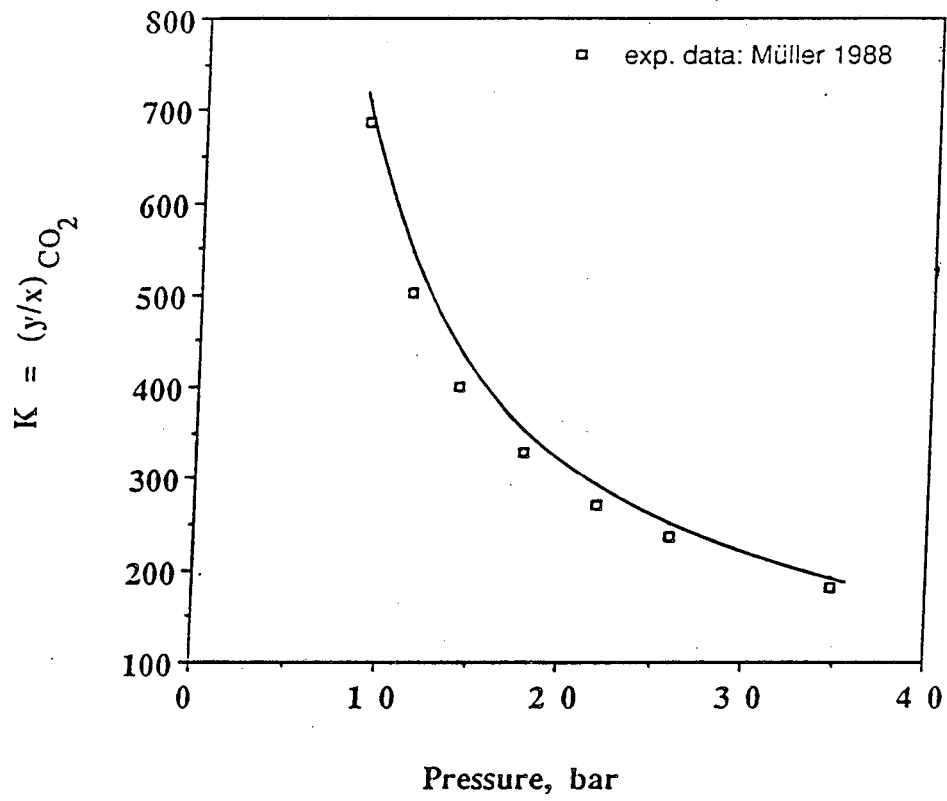


Figure 2: K - Factors for Carbon Dioxide in Water at 160 °C

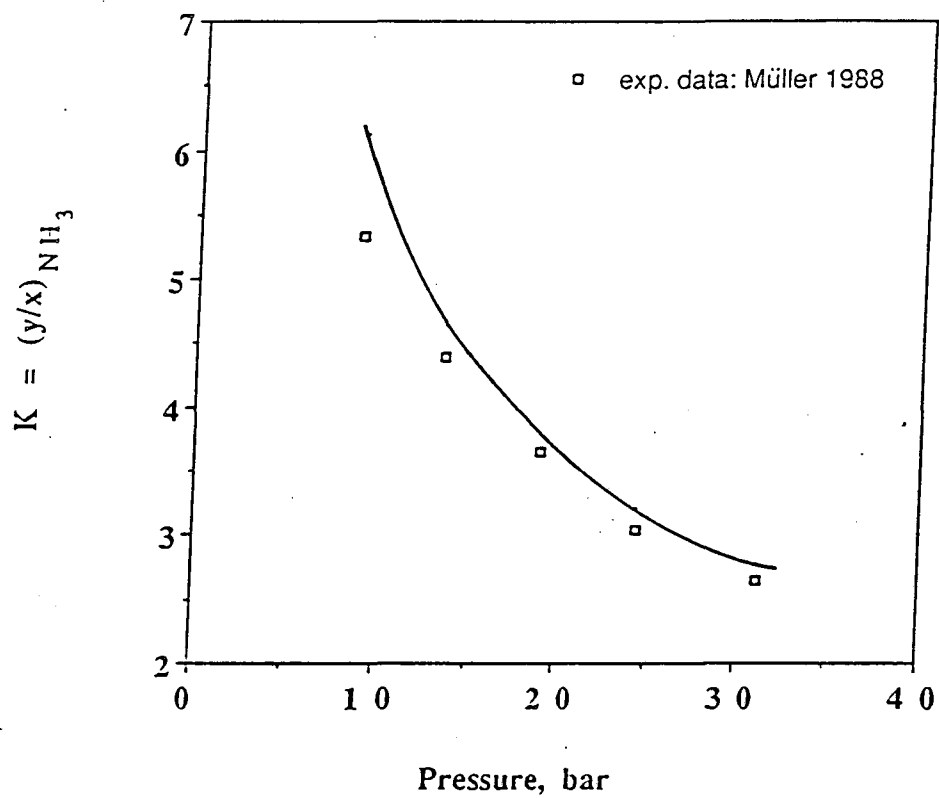


Figure 3: K - Factors for Ammonia in Water at 160 °C

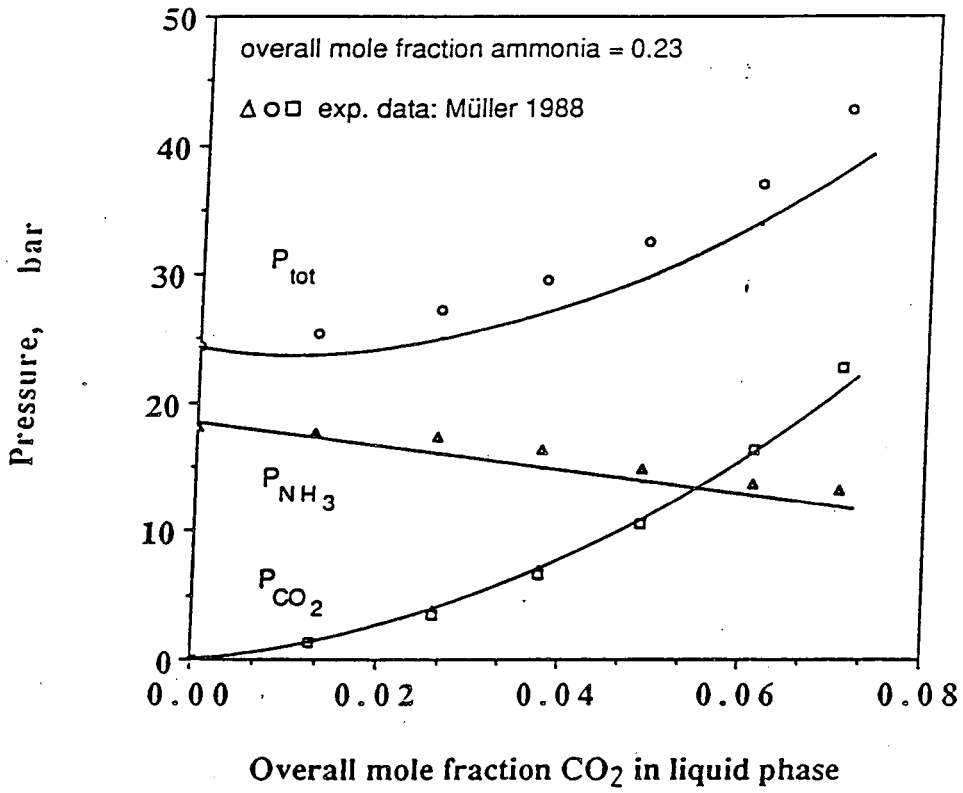


Figure 4: Total and Partial Pressures for Water-Carbon Dioxide-Ammonia at 160 °C

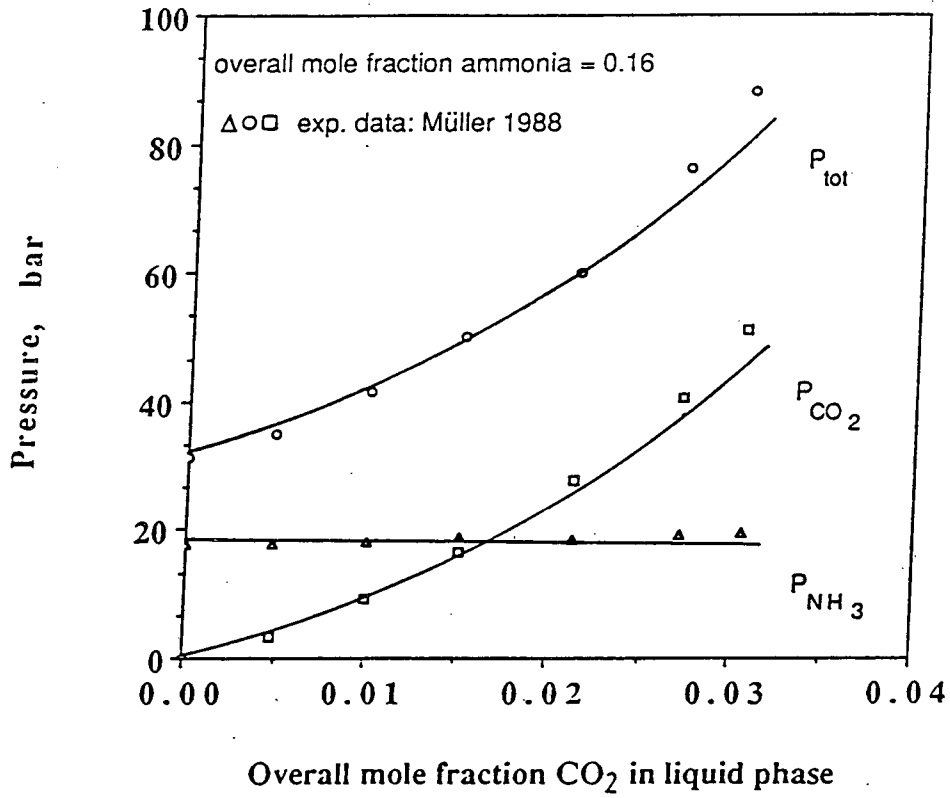


Figure 5: Total and Partial Pressures for Water-Carbon Dioxide-Ammonia at 200 °C

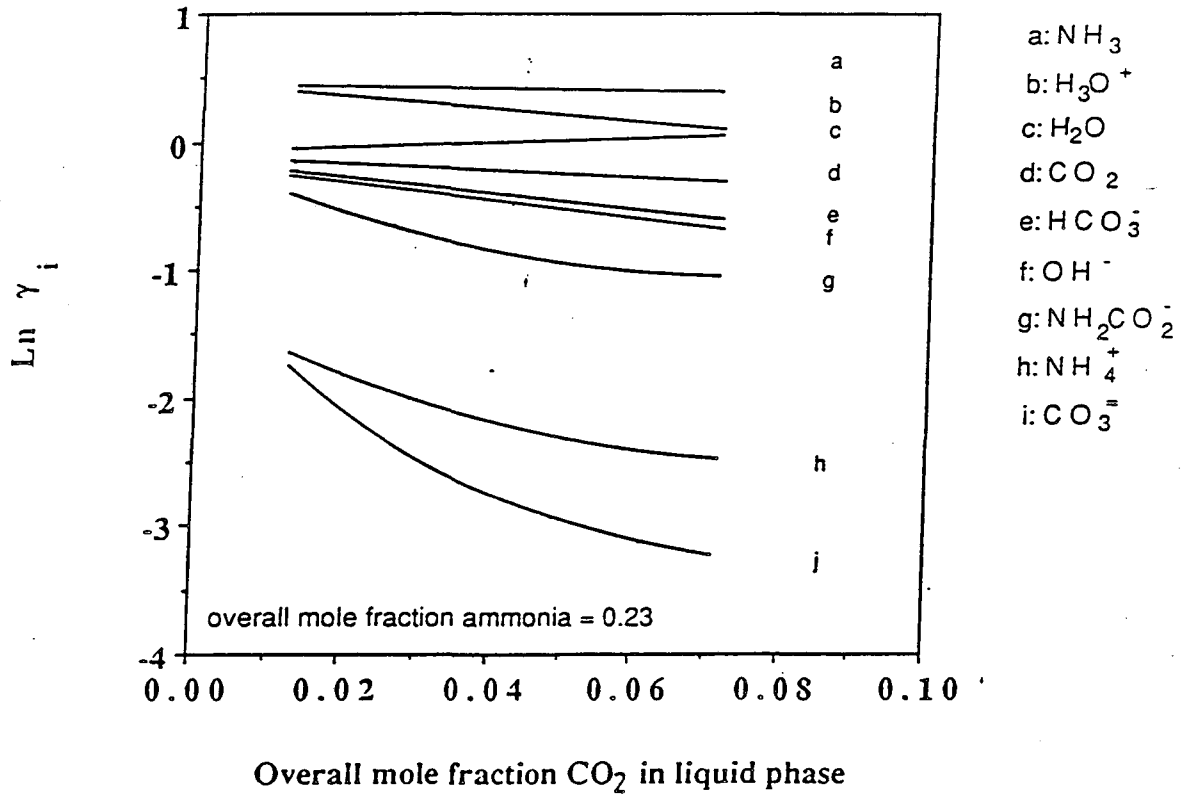


Figure 6: Activity Coefficients for Water-Carbon Dioxide-Ammonia at 160 °C

*LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720*