DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/MIT--360

DE83 014427

Consolidated Fuel Reprocessing Program

VAPOR-LIQUID EQUILIBRIUM OF THE $\text{Mg}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ SYSTEM

Brian E. Thompson
Jeffrey J. Derby
Evelyn H. Stalzer

Oak Ridge Station
School of Chemical Engineering Practice
Massachusetts Institute of Technology
G. A. Huff, Jr. Director

Consultants

R. M. Counce and R. T. Jubin
Fuel Recycle Division

and

R. E. Barker
Chemical Technology Division

Date Published: June 1983

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

Contract No. W-7405-eng-26

CONTENTS

	<u>Page</u>
ABSTRACT	v
1. SUMMARY	1
2. INTRODUCTION	2
2.1 Equilibrium Prediction	2
2.2 Previous Work at ORNL	4
2.3 Objective and Approach	5
3. THEORY	5
3.1 Vapor-Liquid Equilibrium	5
3.2 Reaction Equilibrium	8
3.3 $\text{Mg}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ System	8
4. EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA	10
4.1 Apparatus	10
4.2 Procedure	10
4.3 Results and Discussion	12
5. LITERATURE DATA ON VAPOR-LIQUID EQUILIBRIUM	16
6. CORRELATION OF DATA	17
6.1 Simplified Dissociation Model	17
6.2 Full-Dissociation Model	26
6.3 Pseudobinary Model	33
6.4 Relative-Volatility Correlation	37
7. CONCLUSIONS	40
8. RECOMMENDATIONS	40
9. ACKNOWLEDGMENTS	40
10. APPENDIX	41
10.1 VLE Data	41
10.2 Simplified-Dissociation-Model Calculations	41
10.3 Full-Dissociation-Model Calculations	52
10.4 Calculations for the Pseudobinary Model	55
10.5 Relative Volatility Calculations	56
10.6 Bubble-Point Program	60

	<u>Page</u>
10.7 Model Extension	60
10.8 Location of Data	62
10.9 Nomenclature	63
10.10 References	65

1. SUMMARY

Highly concentrated nitric acid (20-22 M) is used in treating plant off-gases for iodine control (Iodox process) in the processing of spent nuclear fuel. The fuel Recycle Division at Oak Ridge National Laboratory (ORNL) is investigating a two-pot extractive-distillation scheme to reconcentrate the acid with a salt, $\text{Mg}(\text{NO}_3)_2$. To design this system, a vapor-liquid equilibrium (VLE) correlation of the $\text{Mg}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ system is necessary.

Several approaches were tried to correlate VLE data reported by Ginnow and Clark (7), Shneerson et al. (19), Cigna et al. (2) and our own and other work at ORNL. Two approaches were successful.

One approach was to use a simplified dissociation equation:

$$K = \frac{x_{\text{H}^+} x_{\text{NO}_3^-}}{x_{\text{HNO}_3}} \quad (1)$$

in which K is the equilibrium constant and x_i the mole fraction of species i .

The calculated activity coefficients were correlated as a quadratic function of the $\text{Mg}(\text{NO}_3)_2$ and HNO_3 concentrations. The average absolute error in the prediction of the mole fraction of HNO_3 in the vapor phase was 8%, and the average error in the prediction of the bubble-point temperature was 8 K.

The other approach was a full-dissociation model in which the ionic strength and mole fractions were calculated by assuming full dissociation of the HNO_3 and $\text{Mg}(\text{NO}_3)_2$. The functional forms of the activity coefficients were found by defining the excess Gibbs energy as:

$$G^E = G^A + G^B \quad (2)$$

where G^A is a term for the coulombic (ionic) interactions, and G^B is a term for the noncoulombic (molecular) interactions. The average absolute error in the prediction of the mole fraction of HNO_3 in the vapor phase was 9%, and the average absolute error in the prediction of the bubble-point temperature was 10 K.

A pseudobinary approach which accounted for salt effects through the definition of reference-state fugacities and an empirical approach to correlate relative volatilities of HNO_3 and H_2O with $\text{Mg}(\text{NO}_3)_2$ concentration failed to yield satisfactory results.

Further refinement of the two successful models is recommended to combine the favorable aspects of each into one model, which includes the extent of acid dissociation and thermodynamic consistency. The models developed in this study can be used for either design or operation of the two-pot process.

2. INTRODUCTION

Concentrated (20–22 M) nitric acid is proposed for use in treatment of offgases for iodine removal in a nuclear fuel reprocessing facility. The nitric acid can be purified by distillation to an azeotropic concentration of 68 wt %, for a mixture of nitric acid and water. For further concentrations, the Fuel Recycle Division at ORNL has developed a continuous, two-pot, extractive-distillation system, with magnesium nitrate as the solvent (3), as shown in Fig. 1. Nitric acid at a concentration slightly less than azeotropic is mixed with magnesium nitrate in the lower pot. The magnesium nitrate changes the relative volatility of the water and nitric acid so that concentrated nitric acid (about 90 wt %) can be produced as a vapor. The liquid is transferred to the solvent-recovery pot, where dilute nitric acid is evaporated to reconcentrate the $\text{Mg}(\text{NO}_3)_2$. The concentrated $\text{Mg}(\text{NO}_3)_2$ is then recycled to the extractive-distillation pot.

2.1 Equilibrium Prediction

The prediction of equilibrium conditions for the $\text{Mg}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ system is required to design the two-pot process. Several researchers have measured the vapor-liquid equilibrium of this ternary system (2, 7, 15, 19). Although some correlations have been proposed for the data, they cannot accurately be extended to conditions representative of those in the two-pot process.

Some of the VLE correlations for systems containing a salt, such as $\text{Mg}(\text{NO}_3)_2$, are based on the relative volatility as calculated by:

$$\epsilon_{12} = \frac{Y_1 X_2}{X_1 Y_2} \quad (3)$$

where ϵ_{12} is the relative volatility of component 1 with respect to component 2, and X_i and Y_i are the mole fractions of component i (1 or 2) in the liquid and vapor phases, respectively. This ratio gives an indication of the ease of separation of components 1 and 2.

For some systems of two nonelectrolytes and a salt, Johnson and Furter (10) reported that the relative volatility in the salt solution was related to the relative volatility in a system free of salt by:

$$\log \frac{\epsilon_{12}}{\epsilon_{12}^*} = k X_S \quad (4)$$

where X_S is the mole fraction of salt in the liquid, and k is an empirically determined constant.

Hála et al. (9) defined a separation factor β_{12} as:

$$\beta_{12} = (Y_1/Y_2)(X_2/X_1) \quad (5)$$

This parameter is similar to the relative volatility ϵ_{12} . They successfully correlated β_{12} as a function of:

$$\log \beta_{12} = f(I) + f(X_1, X_2) \quad (6)$$

where the ionic strength I is given by:

$$I = \frac{1}{2} \sum_i X_i \left[v_{i+} Z_{i+}^2 + v_{i-} Z_{i-}^2 \right] \quad (7)$$

for the reaction of the electrolyte:

where v is the stoichiometric coefficient and Z is ionic charge.

2.2 Previous Work at ORNL

Work at ORNL has been performed to characterize the basic equilibrium of the salt system and the operation of the two-pot process. Ginnow and Clark (7) recently performed studies on the equilibrium of solutions

with high (60 to 80 wt %) $\text{Mg}(\text{NO}_3)_2$ concentrations. They made no attempt to correlate their data. Experimental work at ORNL undertaken by Counce et al. (3) provided a better understanding of the operation of the two-pot system. An empirical correlation, based on VLE data by Shneerson et al. (19) and Cigna et al. (2) was developed; however, it did not predict the behavior of the solvent recovery pot, which operated outside of the range of the data correlated.

2.3 Objective and Approach

The objective of this work was to characterize the vapor-liquid equilibrium (VLE) of the $\text{Mg}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ system. The data from several literature sources were correlated with thermodynamically based equations. In addition, a batch still was used to obtain VLE data.

3. THEORY

3.1 Vapor-Liquid Equilibrium

The equilibrium state of a closed system at constant pressure and temperature occurs when the total Gibbs energy is at a minimum with respect to all independent variations of the system. This condition is satisfied for a multicomponent system when the chemical potential of each component is the same for all phases. These criteria can be expressed as:

$$T^V = T^L \quad (9)$$

$$p^V = p^L \quad (10)$$

$$\mu_i^V = \mu_i^L \quad (11)$$

where T is temperature, P is total pressure, μ_i is the chemical potential of component i , and the superscripts V and L denote the vapor and liquid phases, respectively.

An alternative method of expressing these criteria was the definition of fugacity. When the temperature and pressure of each phase are equal, the fugacities of each component are the same in both phases at equilibrium:

$$\hat{f}_i^V = \hat{f}_i^L \quad (12)$$

where $\hat{f}_i$ is the fugacity of component i in the mixture.

The fugacity of a component in a vapor mixture can be expressed as:

$$\hat{f}_i^V = y_i \phi_i \pi \quad (13)$$

where y_i is the mole fraction of component i in the vapor phase, ϕ_i is the fugacity coefficient of component i , and π is the total pressure of the system. Similarly, for a component in a liquid mixture:

$$\hat{f}_i^L = x_i \gamma_i f_i^0 \quad (14)$$

where γ_i is the activity coefficient for component i , and f_i^0 is a reference-state fugacity for the liquid component i .

The equilibrium criterion, Eq. (12), is then:

$$y_i \phi_i \pi = x_i \gamma_i f_i^0 \quad (15)$$

If the reference state for the liquid component is chosen as the pure liquid, the vapor- and liquid-phase fugacity are equal when the pure liquid is in equilibrium with the vapor phase above it:

$$f_i^0 = f_i^V = \phi_i^0 p_i^0 \quad (16)$$

where p_i^0 is the vapor pressure of the liquid at the temperature of the system, and ϕ_i^0 is the corresponding fugacity coefficient. Equation (16) is substituted into Eq. (15) to yield

$$y_i \phi_i \pi = x_i \gamma_i \phi_i^0 p_i^0 \quad (17)$$

At pressures less than 0.1 MPa, the fugacity coefficients $\hat{\phi}_i$ and ϕ_i^0 are very nearly equal (20), so that Eq. (17) reduces to:

$$y_i \pi = x_i \gamma_i P_i^0 \quad (18)$$

The activity coefficient of each component γ_i is a function of composition, temperature, and pressure. The pressure-dependence of the activity coefficient is very weak and can be neglected at pressures less than 0.1 MPa (20).

The activity coefficients for the liquid-mixture components are related to the excess Gibbs energy of the solution by:

$$RT \ln \gamma_i = \left[\frac{\partial G^E}{\partial n_i} \right]_{T, P, n_{j \neq i}} \quad (19)$$

where

n = number of moles

R = gas constant

The right-hand side of Eq. (19) is the partial molar value for the excess Gibbs energy of component i in the solution. If the functional form of the excess Gibbs energy of the solution is known, the activity coefficients are obtained by differentiation of the excess Gibbs energy with respect to mole number of each component.

Thermodynamic consistency requires that the functional forms of the excess Gibbs energy and the corresponding activity coefficients satisfy the Gibbs-Duhem equation. The Gibbs-Duhem equation for a system at constant temperature and pressure is expressed in terms of activity coefficients as:

$$\sum_{i=1}^N x_i d \ln \gamma_i = 0 \quad (20)$$

where N is the total number of components.

3.2 Reaction Equilibrium

For a chemical reaction in a single phase in a closed system at constant temperature and pressure, equilibrium is obtained when the total Gibbs energy is minimized with respect to all independent variations of the system. This criterion is satisfied when for all reactions (20):

$$\sum_{i=1}^{N_R} \nu_i \mu_i = 0 \quad (21)$$

where N_R is the total number of species involved in the reaction.

For an electrolyte undergoing dissociation, the following reaction occurs:

When Eq. (21) is expressed in terms of activity coefficients and mole fractions, it takes the form

$$\frac{(\gamma_+^c X_+^c)^{\nu_+} (\gamma_-^c X_-^c)^{\nu_-}}{\gamma_{MA}^c X_{MA}^c} = K_{MA} \quad (23)$$

where γ_+^c , γ_-^c , and γ_{MA}^c are the activity coefficients of the cation, anion, and undissociated electrolyte, respectively, and X_+^c , X_-^c , X_{MA}^c correspond to mole fractions based on the total species in solution. The equilibrium constant K_{MA} is a function only of temperature, and its value depends on the reference states chosen for each of the species involved in the reaction.

3.3 $Mg(NO_3)_2$ - HNO_3 - H_2O System

The equilibrium of a closed system consisting of both electrolytic and nonelectrolytic components must simultaneously satisfy the criteria of phase and reaction equilibria. In such a system, the excess Gibbs energy is a function of temperature, pressure, and composition. This dependence must account for molecule-molecule, ion-molecule, and ion-ion interactions. The magnesium nitrate-nitric acid-water system has two electrolytes, the magnesium salt and nitric acid.

If hydration of the undissociated species is neglected, the major liquid-phase reactions are the dissociation of the two electrolytes:

The criteria for reaction equilibria at constant temperature and pressure are:

$$\frac{(\gamma_{\text{H}^+} x_{\text{H}^+})(\gamma_{\text{NO}_3^-} x_{\text{NO}_3^-})}{\gamma_{\text{HNO}_3} x_{\text{HNO}_3}} = K_A \quad (26)$$

and

$$\frac{(\gamma_{\text{Mg}^{2+}} x_{\text{Mg}^{2+}})(\gamma_{\text{NO}_3^-} x_{\text{NO}_3^-})^2}{\gamma_{\text{Mg}(\text{NO}_3)_2} x_{\text{Mg}(\text{NO}_3)_2}} = K_S \quad (27)$$

If the activity coefficients of each species and the equilibrium constants are known, the resulting equations can be solved to find the extent of dissociation of both the salt and the acid in the liquid phase. In this study, gas-phase reactions were assumed not to occur.

In addition to the reaction equilibria described by Eqs. (26) and (27), equilibrium must occur between the gas and liquid phases. From Eq. (20), the equations describing this equilibrium are:

$$y_{\text{H}_2\text{O}} \pi = x_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^0 \quad (28)$$

$$y_{\text{HNO}_3} \pi = x_{\text{HNO}_3} \gamma_{\text{HNO}_3} P_{\text{HNO}_3}^0 \quad (29)$$

It is assumed that no magnesium nitrate is present in the gas phase.

If the activity coefficients are known, Eqs. (26) to (29) can be used to predict vapor-phase compositions if temperature, pressure, and liquid phase composition are given. These activity coefficients are complex functions of composition and temperature because they must account for both coulombic and noncoulombic interactions. The prediction of vapor-liquid equilibrium in an electrolyte system is therefore very difficult.

4. EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA

4.1 Apparatus

A batch still was used to obtain the vapor-liquid equilibrium data, as shown in Fig. 2. A 1000-ml glass flask with three ground-glass necks was used. A thermometer was placed in one neck of the flask, with the bulb completely immersed in the liquid. A glass adapter fitted with a thermometer was placed in the central neck, with the thermometer bulb located at the base of the flask neck. The adapter was connected to a chilled-water condenser. The third neck of the flask, fitted with a ground-glass stopper, was used as a liquid-sampling port. A heating mantle surrounded the bottom of the flask. Glass beads and a magnetic stirring bar were used in the flask to facilitate boiling. The flask was well insulated from the edge of the mantle to the top of the adapter. The insulation was arranged so that a small section near the base could be moved, so that boiling could be observed. A 10-ml pipette and glass vials were used for sampling the liquid mixture.

4.2 Procedure

The procedure described below was followed for each run on the batch still.

Glass beads and a magnetic stirring bar were added to the 1000-ml, three-neck flask. A known weight of magnesium nitrate in the hexahydrate form, $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, was added to the flask, followed by a known volume of azeotropic (68 wt %) HNO_3 . The weights of $\text{Mg}(\text{NO}_3)_2$ ranged from 350 to 425 g, and the acid volumes from 60 to 250 ml. The condenser water was turned on and the flask insulated. The variac was turned to 100 VAC to begin heating and lowered to approximately 65 VAC when the liquid temperature reached 373 K. Condensate was collected at intervals of 5 K up to 448 K. The temperature increase during collection was less than 1 K. Condensate sample volume ranged from 1 to 10 ml, depending on temperature and initial amounts of $\text{Mg}(\text{NO}_3)_2$ and HNO_3 . After the last drop of condensate was collected, the glass stopper was removed to pipette 5 to 8 ml of the boiling liquid into a glass vial. The liquid was not sampled during condensate-collection because sampling required removal

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

BATCH STILL

DATE
07/19/82

DRAWN BY
EHS

FILE NO.
CEPS-X-360

FIG.
2

of the glass stopper, which permitted vapor loss to the atmosphere. A run took between 1.5 and 2.5 h, depending upon the initial charge.

Two runs were made on the experimental equipment by J. L. Marley of ORNL. Another run was made by the authors.

Acid composition was determined within 2 wt % by thermal titration. Magnesium nitrate composition was determined within 1.6 wt % by titration with ethylenediaminetetraacetate (EDTA) as the chelating agent and Eriochrome Black T, an azo dye, as the indicator.

4.3 Results and Discussion

The mixture was observed to boil vigorously during the run. A temperature difference between liquid and vapor was noted. The difference was about 5 K when condensate was first produced and increased to about 40 K by the end of the run, when the $\text{Mg}(\text{NO}_3)_2$ concentration in the liquid was at its highest. This temperature difference was also reported by Cigna et al. (2). The other investigators did not report vapor temperature. When the batch still was operated with pure water, a temperature difference of less than 0.1 K was observed. No explanation is offered for the larger temperature difference in the ternary system. The temperatures and composition of liquid and vapor phases are reported in Tables 1 through 6 in Appendix 10.1. The liquid-phase compositions are shown on a ternary diagram in Fig. 3. The small triangle containing the experimental data is expanded in Fig. 4 and includes values for the vapor-phase weight percentage of acid. The ORNL data of Fig. 4 follow the same trend as that reported by Shneerson et al. (19), as seen in Fig. 5. For two points of the data, the reported liquid-phase weight percentage of the acid was negative; these points are not included in the figures. The vapor samples corresponding to these liquid samples showed the presence of HNO_3 at about 10 wt %. In both cases, the acid-deficient liquid occurred at the end of a run. It is postulated that once the original nitric acid had volatilized as vapor and condensed, the $\text{Mg}(\text{NO}_3)_2$ and H_2O reacted to form HNO_3 . As this newly produced acid was volatilized, the residue became acid-deficient, which probably resulted in the formation of magnesium hydroxide, $\text{Mg}(\text{OH})_2$, as:

Evidence for this comes from the operation of a bench-scale, two-pot process at ORNL. During startup, the system was operated with only $\text{Mg}(\text{NO}_3)_2$ and H_2O . Plugging occurred; analysis of the solid showed it to consist of 80 to 98 wt % $\text{Mg}(\text{OH})_2$.

5. LITERATURE DATA ON VAPOR-LIQUID EQUILIBRIUM

Several researchers obtained vapor-liquid equilibrium (VLE) data for the $\text{Mg}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ system (2, 7, 15, 19). All the data for the ternary system were acquired at atmospheric pressure (0.101 MPa). Values for the temperature and the liquid and vapor compositions of boiling solutions were recorded (see Tables 1 through 6 in Appendix 10.1).

Most of the data were taken with vapor-recirculating batch stills. Shneerson et al. (19) used this apparatus, equipped with a manostat to maintain atmospheric pressure. The binary system $\text{HNO}_3\text{-H}_2\text{O}$ was used to test the equipment. Ginnow and Clark (7) used a modified Othmer still. Heating tape was placed on the upriser to prevent condensation on the walls. Cigna et al. (2) also used an Othmer still. No description of the experimental apparatus used by Prosek (15) was given.

The compositions of the systems ranged from 0 to 70 wt % $\text{Mg}(\text{NO}_3)_2$ and 0 to 75 wt % HNO_3 . The data from Shneerson et al. (19) covered most of this range, with the exception of the binary systems $\text{Mg}(\text{NO}_3)_2\text{-H}_2\text{O}$ and $\text{HNO}_3\text{-H}_2\text{O}$. Ginnow and Clark (7) acquired VLE data for $\text{Mg}(\text{NO}_3)_2$ concentrations greater than 60 wt % and HNO_3 concentrations less than 20 wt %. Cigna et al. (2) determined the data for about the same range as Shneerson et al. (19), with the addition of the $\text{Mg}(\text{NO}_3)_2\text{-H}_2\text{O}$ system up to 68 wt % $\text{Mg}(\text{NO}_3)_2$. Prosek (15) reported data in a smaller range of about 10 to 35 wt % $\text{Mg}(\text{NO}_3)_2$ and 1 to 6 wt % HNO_3 .

The data taken by Shneerson et al. (19), Cigna et al. (2), and Ginnow and Clark (7) show the same general trends. The weight percentage of HNO_3 in the vapor is shown as a function of the liquid composition for the data of Shneerson et al. on the ternary diagram in Fig. 5. The HNO_3 vapor concentration increased as $\text{Mg}(\text{NO}_3)_2$ was added to a system containing a constant $\text{HNO}_3\text{-to-H}_2\text{O}$ ratio. The only notable differences between the data from Shneerson et al., Cigna et al., and Ginnow and Clark are the additional scatter in the data of Ginnow and Clark and a disagreement in the vapor-phase compositions for the region of about 60 wt % $\text{Mg}(\text{NO}_3)_2$ and 2 to 6 wt % HNO_3 . For instance, at 2.8 wt % HNO_3 and 60 wt % $\text{Mg}(\text{NO}_3)_2$ in the liquid, Cigna et al. observed a vapor concentration of 13.1 wt % HNO_3 ; at 2.8 wt % HNO_3 and 59.3 wt % $\text{Mg}(\text{NO}_3)_2$ in the liquid, Shneerson et al. reported a vapor composition of 46.1 wt %. The concentrations reported by Shneerson et al. in mole fractions are not consistent with the concentrations reported in weight fractions, with inconsistencies as great as 3%.

6. CORRELATION OF DATA

6.1 Simplified Dissociation Model

6.1.1 Model Development

Equilibrium for the dissociation of HNO_3 [Eq. (24)] is expressed as:

$$K_A = \frac{(\gamma_{A+} X_{A+})(\gamma_{-} X_{-})}{\gamma_A X_A} \quad (31)$$

where X_{A+} is the mole fraction of the hydrogen ion, X_{-} is the mole fraction of the nitrate ion, and X_A is the mole fraction of the undissociated nitric acid. These mole fractions are based on the total number of moles present in solution. The γ values are the activity coefficients based on the mole fractions of total species. The vapor equilibrium is given by Eq. (17) for the acid and water.

VLE data available for the $\text{Mg}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ system are vapor composition and bubble-point temperature at atmospheric pressure (0.101 MPa) for different liquid-phase compositions. The activity coefficients γ_A and γ_w are not directly calculated from Eq. (17) because X_A and X_w cannot be estimated until the extent of dissociation of the acid is known. The extent of dissociation can be obtained from Eq. (31) if the activity coefficients of all the species are known; however, it is not possible to independently measure these quantities. If a functional form for the activity coefficients is assumed, it is possible to fit the parameters with experimental data and Eqs. (17) and (31). The reaction equilibrium is approximated in this approach by:

$$K_A = \frac{X_{A+} X_{-}}{X_A} \quad (32)$$

This form is obtained from Eq. (31) when $\gamma_{A+} \gamma_{-} / \gamma_A = 1$, which is a close approximation at low acid concentrations. At high acid concentrations, the extent of dissociation cannot be accurately predicted. However, the behavior of the acid in solution is still more closely approximated by this approach than by the assumption of either complete or no dissociation.

The mole fractions of the total species can be expressed in terms of the analytical mole fractions and the extent of nitric acid dissociation α . Complete dissociation of the magnesium nitrate is assumed so:

$$X_{A+}' = \frac{\alpha X_A}{1 + \alpha X_A + 2X_S} \text{ for the hydrogen ion ,} \quad (33)$$

$$X_{-}' = \frac{\alpha X_A + 2X_S}{1 + \alpha X_A + 2X_S} \text{ for the nitrate ion ,} \quad (34)$$

$$X_A' = \frac{(1 - \alpha)X_A}{1 + \alpha X_A + 2X_S} \text{ for the undissociated acid ,} \quad (35)$$

$$X_W' = \frac{X_W}{1 + \alpha X_A + 2X_S} \text{ for water .} \quad (36)$$

An unprimed X refers to the analytical mole fraction, which is defined by the number of moles of the pure compounds added to the solution, based on the assumption of no dissociation. These mole fractions of total species are substituted into Eq. (32) to yield:

$$K_A = \frac{\alpha^2 X_A + 2\alpha X_S}{(1 + \alpha X_A + 2X_S)(1 - \alpha)} \quad (37)$$

The equilibrium constant is expressed as

$$K_A = \bar{A} e^{-\Delta H/RT} \quad (38)$$

where $\bar{A}$ is a constant, and ΔH is the heat of reaction.

If $\bar{A}$ and ΔH are independent of temperature, a value of the equilibrium constant can be predicted with Eq. (38). Values of $\bar{A}$ and ΔH were determined to be 0.0015 and 2900 cal/mol, respectively, as detailed in Appendix 10.2.

For a given system temperature, a value for K_A was calculated from Eq. (38), and the extent of dissociation was determined from Eq. (37). Once the extent of dissociation α was known, Eqs. (35) and (36) were used to calculate X_A' and X_W' . Pure-component vapor pressures were estimated with the Antoine equations for nitric acid and water, and experimental activity coefficients were determined from Eq. (17).

The Antoine equations are (6, 17):

$$\log_{10} p_w^0 \text{ (Pa)} = 10.074 - \frac{1657.4}{T-46.2} \quad (39)$$

$$\log_{10} p_w^0 \text{ (Pa)} = 9.741 - \frac{1486.2}{T-43.3} \quad (40)$$

The Antoine equation for water is valid from 284 to 441 K (17). The range of the nitric acid Antoine equation is 263 to 373 K. However, this equation was used for the higher temperatures of the $\text{Mg}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ system because vapor pressure information for nitric acid at higher temperatures is unavailable. The use of Eq. (40) to define the reference state for nitric acid should not cause any difficulties in its extrapolation to higher temperatures. The reference state is defined for the pure component at atmospheric pressure and 273 K. Equation (40) should be used to predict vapor-phase composition if the value of the activity coefficient is given.

The activity coefficients are functions of liquid-phase composition, temperature, and pressure. The temperature of the system is a function of composition and pressure because the ternary data of the $\text{Mg}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ system are given for boiling solutions:

$$T = T(X_A, X_W, P) \quad (41)$$

If the pressure is specified as atmospheric (0.101 MPa), the activity coefficients depend only on liquid composition:

$$\gamma_A' = \gamma_A'(X_A, X_S) \quad (42)$$

$$\gamma_W' = \gamma_W'(X_A, X_S) \quad (43)$$

The logarithms of the activity coefficients were approximated by a second-order polynomial expansion in X_A and X_S as:

$$\ln \gamma_i' = A_{i0} + A_{i1}X_A + A_{i2}X_A^2 + A_{i3}X_S + A_{i4}X_S^2 + A_{i5}X_AX_S \quad (44)$$

There are six parameters in the expressions for both the nitric acid and water activity coefficients, or a total of 12 parameters. Eight of these were fit with binary data for $\text{HNO}_3\text{-H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2\text{-H}_2\text{O}$ systems. The remaining four constants were fit with ternary data from the work of Schneerson et al. (19) and Cigna et al. (2). The data of Ginnow and Clark (7) were not used because of their greater scatter. The data of Prosek (15) were clearly in disagreement with the data from the other studies and were not used for the regression of parameters, as discussed in Appendix 10.2.

The final form of the activity coefficients was determined to be:

$$\ln \gamma'_W = -0.17 X_A - 3.62 X_A^2 - 4.47 X_S - 15.38 X_S^2 - 28.2 X_A X_S \quad (45)$$

$$\ln \gamma'_A = -2.52 + 6.21 X_A - 3.10 X_A^2 + 23.83 X_S - 24.20 X_S^2 - 15.80 X_A X_S \quad (46)$$

The parameters of both equations are useful in explaining the physical behavior of the $\text{Mg}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ system. It is known that the volatility of water is reduced ("salting out") by the addition of magnesium nitrate to the binary acid-water system. The negative parameters of Eq. (45) cause water to exhibit this trend. Because the vapor composition of water is proportional to its activity coefficient, an increase of either salt or acid concentration decreases γ'_W , which decreases the vapor-phase concentration of water. Because all the parameters of Eq. (45) are negative, the activity coefficient of water approaches 1 for pure water only; for all other compositions, γ'_W is less than 1. The parameters of the activity coefficient for nitric acid [Eq. (46)] are both positive and negative. The predominant terms of the expression are those first-order in mole fraction because X_A and X_S are always less than or equal to 1. The coefficients of these terms are positive, which is also characteristic of the ternary system; when salt or acid concentrations are increased, the fraction of HNO_3 in the vapor also increases. The positive first-order parameters represent this physical behavior; the acid activity coefficient increases with increasing acid or salt concentration. This effect causes the azeotrope to disappear at high salt concentrations (>40 wt %).

6.1.2 Results and Discussion

For a given temperature and liquid-phase composition, the extent of dissociation of nitric acid, total species mole fractions, and activity coefficients were predicted from Eqs. (35) to (37), (43), and (44). This information was used with the VLE criteria and Antoine equations for the pure components to obtain the vapor-phase composition.

The data used in this study were from boiling systems at atmospheric pressure. From a bubble-point calculation, vapor composition and temperature for these experimental data were predicted. The bubble-point program is described in Appendix 10.6.

The vapor compositions and temperatures predicted by the model are shown as a function of the experimentally determined values in Figs. 6 and 7, respectively. The experimental data included on these plots are those obtained by Ginnow and Clark (7), Schneerson et al. (19), Cigna et al. (2), Marley (12), and us. There is good agreement between the predicted and experimental values.

Residuals of the predictions for the different data sets are listed in Tables 1 through 6 in Appendix 10.1. Plots of predicted and experimental values for the individual data sets are given in Appendix 10.2.3. Examination of residuals for both vapor-phase composition and bubble-point temperature showed no significant trends.

In general, the major disagreement between predicted and experimental vapor-phase composition occurred in the region of approximately 60 wt % $\text{Mg}(\text{NO}_3)_2$ and between 2 to 6 wt % HNO_3 . Predicted vapor weight fractions of nitric acid are about 20 wt % higher than experimental values given in this region by Cigna et al. (2), and approximately 5 to 10 wt % lower than the values given by Schneerson et al. (19). More experimental data for this region are necessary to determine the correct vapor-phase composition values.

The major error in the predicted and experimental bubble-point temperatures was also in the region of about 70 wt % $\text{Mg}(\text{NO}_3)_2$ and 10 wt % HNO_3 . Values given by Ginnow and Clark do not agree with predicted values. The predicted temperatures of about 373 to 378 K disagreed with the experimental values of 410 to 445 K.

Predicted HNO_3 vapor concentration is plotted as a function of liquid composition expressed on a salt-free basis for constant $\text{Mg}(\text{NO}_3)_2$ concentrations in Fig. 8. The solid curves indicate regions where experimental data were taken, and the dashed curves indicate extrapolation into regions where presently no data exist. The azeotrope of the binary HNO_3 - H_2O mixture is given by the intersection of the zero wt % $\text{Mg}(\text{NO}_3)_2$ curve with the $Y = X$ line. The predicted azeotrope is at 68 wt % nitric acid. This is in very good agreement with reported azeotrope composition of 68.3 wt % (19). For 30 wt % $\text{Mg}(\text{NO}_3)_2$, an azeotrope occurs at about 28 wt % HNO_3 on a salt-free basis. This value is close to the values of 31.7 wt % HNO_3 reported by Schneerson et al. (19) and 30 wt % HNO_3 observed by Cigna et al. (2) for the azeotrope of this system. The model predicts disappearance of the azeotrope at about 43 wt % of $\text{Mg}(\text{NO}_3)_2$.

Predicted temperature curves as functions of wt % $\text{Mg}(\text{NO}_3)_2$ and liquid phase weight fraction of HNO_3 on a salt-free basis are plotted in Fig. 9. The maximum of the 0 wt % curve corresponds to the predicted azeotropic temperature. The predicted value is within 1 K of the actual boiling point of the azeotrope (393 K) at atmospheric pressure.

- ▲ Thompson et al. (this paper)
- ▼ Marley (12)
- Shneerson et al. (19)
- ✕ Cigna et al. (2)
- ◆ Ginnow and Clark (7)

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

PREDICTED VS EXPERIMENTAL VAPOR-PHASE
COMPOSITION - SIMPLIFIED
DISSOCIATION MODEL

DATE
07/25/82

DRAWN BY
EHS

FILE NO.
CEPS-X-360

FIG.
6

- ▲ Thompson et al. (this paper)
- ▼ Marley, 1982 (12)
- Shneerson et al. (19)
- ◆ Cigna et al. (2)

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

BUBBLE-POINT TEMPERATURE - SIMPLIFIED
DISSOCIATION MODEL

DATE 07/25/82	DRAWN BY EHS	FILE NO. CEPS-X-360	FIG. 7
------------------	-----------------	------------------------	-----------

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

VAPOR COMPOSITION AS A FUNCTION OF
LIQUID COMPOSITION - SIMPLIFIED
DISSOCIATION MODEL

DATE
07/24/82

DRAWN BY
EHS

FILE NO.
CEPS-X-360

FIG.
8

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

PREDICTED BUBBLE-POINT TEMPERATURE AS A
FUNCTION OF LIQUID COMPOSITION
SIMPLIFIED DISSOCIATION MODEL

DATE

07/25/82

DRAWN BY

EHS

FILE NO.

CEPS-X-360

FIG.

9

This model predicted vapor-phase composition and bubble-point temperature for the ternary system with an average absolute deviation of 8 mole % and 8 K, respectively. The explanation for this good agreement is the accurate estimation of the effects of the nitric acid dissociation on the vapor-liquid equilibrium. However, this model does not satisfy the Gibbs-Duhem equation and is therefore not thermodynamically consistent. The predicted bubble-point temperatures at nitric acid concentrations above 95 wt % are negative, so the model is physically unrealistic in this region.

6.2 Full-Dissociation Model

6.2.1 Model Development

The classical approach to the study of electrolytic solution thermodynamics involves the assumption of complete dissociation of all electrolytic species (5, 8, 11, 18). Although this assumption is only valid for a strong electrolyte at infinite dilution, it does not lead to any thermodynamic inconsistencies.

Equation (23) must be satisfied for all dissociation reactions in the $\text{Mg}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ system. For HNO_3 , Eq. (31) is applicable. The quantities $\gamma_{\pm}^{\sim}$, $\gamma_{\pm}^{\sim}$ and $X_{\pm}^{\sim}$, $X_{\pm}^{\sim}$ cannot be measured independently; a mean ionic activity coefficient and a mean ionic molarity must be defined as:

$$\gamma_{\pm} = (\gamma_{A+}^{\sim} \gamma_{-}^{\sim})^{1/2} \quad (47)$$

$$X_{\pm} = (X_{A+}^{\sim} X_{-}^{\sim})^{1/2} \quad (48)$$

to describe the properties of the undissociated nitric acid. These mean ionic quantities are substituted into Eq. (31) to yield:

$$\frac{\gamma_{\pm}^2 X_{\pm}^2}{K} = \gamma_A^{\sim} X_A^{\sim} \quad (49)$$

The VLE criterion for nitric acid is expressed as:

$$Y_{A\pi} = \gamma_A^{\sim} X_A^{\sim} P_A^0 \quad (50)$$

Equation (49) is substituted into Eq. (50) to yield:

$$Y_{A^{\pi}} = \frac{\gamma_{\pm}^2 X_{\pm}^2}{K_A} P_A^0 \quad (51)$$

If full dissociation is assumed, the mean ionic molarity is determined from Eqs. (33) and (34). Both X_{A+} and X_{-} are determined for full dissociation ($\alpha = 1$) to yield:

$$X_{\pm} \equiv (X_{A+} X_{-})^{1/2} = \left[\frac{X_A (X_A + 2X_S)}{(1 + X_A + 2X_S)^2} \right]^{1/2} \quad (52)$$

For the assumption of full dissociation, the mean ionic activity coefficient has the form of a mean rational activity coefficient. The effects of differing extents of dissociation in the system are included in this mean rational activity coefficient,

$$\gamma_{i\pm} = \frac{a_{i\pm}}{X_{i\pm}^v} \quad (53)$$

At a given temperature, the value of K_A depends on the reference states chosen for each species. These reference states are chosen for nitric acid so that the mean rational activity coefficient $\gamma_{\pm}$ approaches unity as the mole fraction of nitric acid approaches unity. The mean ionic molarity $X_{\pm}$ approaches 0.5 as the analytical mole fraction of nitric acid X_A approaches unity, because complete dissociation was assumed.

For the reference states chosen in this manner, Eq. (51) becomes:

$$Y_{A^{\pi}} = 4 \gamma_{\pm}^2 X_{\pm}^2 P_A^0 \quad (54)$$

The corresponding VLE equation for water is:

$$Y_{w^{\pi}} = \gamma_w' X_w' P_w^0 \quad (55)$$

Because of the complete dissociation assumption, the mole fraction of water takes the form [from Eq. (36) when $\alpha = 1$]:

$$X_W = \frac{X_W}{1 + X_A + 2X_S} \quad (56)$$

Equations (54) and (55) are used with experimental VLE data to calculate mean rational activity coefficients, and these activity coefficients can be correlated if a functional form is assumed.

Hála (8) assumed complete dissociation of all electrolytic species and postulated a form for the excess Gibbs energy of mixing. He assumed that the excess Gibbs energy could be expressed by two terms:

$$G^E = G^A + G^B \quad (2)$$

where G^A accounts for the coulombic interactions in the solution because of the presences of ionic species; and G^B represents the effects of noncoulombic molecular interactions.

Hála proposed that the coulombic term of the excess Gibbs energy could be expressed by a power-series expansion of ionic strength as:

$$G^A = bI + cI^{3/2} + dI^2 + \dots \quad (57)$$

where

$$I \equiv \frac{1}{2} \sum_{i=1}^N X_i (v_{i+} Z_{i+}^2 + v_{i-} Z_{i-}^2) \quad (7)$$

where I is the ionic strength, v_{i+} and v_{i-} are the ionic stoichiometry coefficients, Z_{i+} and Z_{i-} are the charges of the ions, and X_i is the analytical mole fraction of species i . Only the first term of this expression is important for dilute solutions. However, the first three terms of this expansion were used because the region of interest of the $\text{Mg}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ system is characterized by high salt concentrations.

A simple form for the noncoulombic term of the excess Gibbs energy is the "second suffix" approximation of Hála (8). This form assumes that G^B is a well-behaved function of the analytical mole

fractions of the solution. For the ternary system of this study, this function is expressed as:

$$G^B = B_S X_S + C_A X_A + B_{SA} X_S X_A + B_{SW} X_S X_W + B_{AW} X_A X_W \quad (58)$$

With the form of the excess Gibbs energy given by $G^A + G^B$, rational activity coefficients for the water and acid are obtained by differentiation of the excess Gibbs energy with respect to mole number holding temperature, pressure, and all other mole numbers constant [Eq. (19)]. The rational activity coefficients take the form:

$$\ln \gamma_{\pm}^2 = B_1 + c \left(\frac{3}{2} I^{1/2} - \frac{1}{2} I^{3/2} \right) + d(2I - I^2) + B_{SA} X_S + B_{AW} X_W \quad (59)$$

$$\ln \gamma'_W = -\frac{1}{2} c I^{3/2} - dI^2 + B_{AW} X_A + B_{SW} X_S \quad (60)$$

where

$$B_1 = b + B_S$$

Although these equations were derived for conditions of constant temperature, they can also be used for isobaric conditions (8). At isobaric conditions, the system is always at its bubble point, so the temperature is no longer an independent variable but is a function of composition and pressure.

The ternary data of Schneerson et al. (19) and Cigna et al. (2) were used to fit the six constants of Eqs. (59) and (60). The resulting equations for the rational activity coefficients were:

$$\ln \gamma_{\pm}^2 = -5.145 + 1.405 \left(\frac{3}{2} I^{1/2} - \frac{1}{2} I^{3/2} \right) + 4.062 (2I - I^2) - 1.745 X_S + 1.989 X_W \quad (61)$$

$$\ln \gamma'_W = -1.405 \left(\frac{1}{2} I^{3/2} \right) - 4.062 I^2 + 1.989 X_A - 1.459 X_S \quad (62)$$

where

$$I = X_A + 3X_S$$

Sample calculations and details on the correlation of the data are shown in Appendix 10.2.

The parameters of the full-dissociation model lend insight into the physical behavior of the ternary system. Except for the coefficient of the X_A term, all parameters of $\ln \gamma_w$ [Eq. (62)] are negative. The ionic strength is a linear combination of the mole fractions of acid and salt; at the higher concentrations of acid and salt, the ionic strength can be greater than 1. At these conditions the first two terms of Eq. (62) dominate, and the activity coefficient of water decreases with increasing acid or salt concentration. These effects produce the reduced volatility ("salting out") phenomenon for water. The expression for $\ln \gamma_{\pm}^2$ [Eq. (61)] is more complicated than the expression for $\ln \gamma_w$; however, trends are still identifiable. The two terms involving ionic strengths are positive quantities and approach zero as either the mole fraction of salt or acid approaches 1. This causes the mean rational activity coefficient to increase with increasing ionic strength. The vapor-phase composition of HNO_3 therefore increase with increasing salt or acid concentration. One effect of this behavior is the disappearance of the azeotrope with this model at higher salt concentrations (>45 wt %). Although this activity coefficient for water is always less than 1, the mean ionic rational activity coefficient for nitric acid can be less than or greater than 1.

6.2.2 Results and Discussion

The system of equations for this model was used to predict equilibrium gas-phase composition at a given temperature. For a given pressure, bubble-point calculations were performed to predict both temperature and vapor-phase composition. This approach was used to predict equilibrium values for the experimental data from liquid-phase composition.

Predicted vapor-phase composition plotted as a function of experimental vapor-phase composition is shown in Fig. 10. Predicted temperature plotted as a function of experimental temperature is shown in Fig. 11. Literature data and our data are included in these plots. There is good agreement between predicted and experimental vapor-phase compositions. However, there is a definite trend exhibited in the predicted and experimental temperature plot. The model underpredicts system temperature at the lower experimental temperatures (less than approximately 400 K) and overpredicts temperature at higher experimental temperatures (greater than approximately 400 K). These deviations probably occur because of the inability of the implicit temperature dependence of the model parameters to handle a large temperature range. Residuals of predicted values are listed in Tables 1 to 6 of Appendix 10.1. Plots of predicted and experimental vapor-phase composition and temperature for individual data sets are shown in Appendix 10.3.3.

●/ Ginnow and Clark (7)

● Schneerson (19)
Chigna (2)

▼ Marley (12)

▲ Thompson et al.
(this paper)

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

PREDICTED VS EXPERIMENTAL VAPOR
COMPOSITIONS - FULL-
DISSOCIATION MODEL

DATE
07/25/82

DRAWN BY
EHS

FILE NO.
CEPS-X-360

FIG.
10

● Ginnow and Clark (7)

● Schneerson (19)
Cigna (2)

▼ Marley (12)

▲ Thompson et al.
(this paper)

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

PREDICTED TEMPERATURE AS A FUNCTION OF
EXPERIMENTAL TEMPERATURE -- FULL-
DISSOCIATION MODEL

DATE
07/25/82

DRAWN BY
EHS

FILE NO.
CEPS-X-360

FIG.
11

The largest disagreement between predicted and experimental vapor-phase composition exists in the region of 60 to 70 wt % $\text{Mg}(\text{NO}_3)_2$ and 5 to 10 wt % HNO_3 . However, this error is generally less than 10 wt % HNO_3 vapor composition. The predicted temperatures of this region also exhibited the greatest deviation from experimental temperatures with values that are 20 to 30 K too high.

Predicted equilibrium curves of nitric acid vapor-concentration plotted as a function of liquid composition on a salt-free basis are shown in Fig. 12 for several concentrations of $\text{Mg}(\text{NO}_3)_2$ in the liquid phase. The dashed curves indicate where the model was extrapolated to regions where present data exist. For the HNO_3 - H_2O system, an azeotrope is predicted at about 63 wt % HNO_3 , which is close to the experimental value of 68.3 wt %. For 30 wt % $\text{Mg}(\text{NO}_3)_2$, an azeotrope of approximately 30 wt % HNO_3 is predicted. This agrees well with values of 31.7 and 30 wt % HNO_3 reported for this salt concentration by Schneerson (19) and Cigna (2), respectively. The azeotrope is predicted by the model to disappear at about 45 wt % $\text{Mg}(\text{NO}_3)_2$.

Predicted temperature curves are plotted as a function of liquid-phase weight fraction of HNO_3 on a salt-free basis for various concentrations of $\text{Mg}(\text{NO}_3)_2$ in Fig. 13. The azeotrope for 0 wt % salt appeared as the maximum of that temperature curve. The predicted temperature was approximately 380 K; the experimental value for this azeotrope is 393 K.

The full-dissociation model predicted vapor-phase values within an average absolute deviation of 9 wt %; predicted bubble-point temperatures showed a 10 K average absolute deviation. The effects of varying degrees of dissociation of electrolytes in solution are not explicitly accounted for in this model. A good fit was obtained although there is an identifiable trend in the bubble-point temperature residuals. The full-dissociation model is thermodynamically consistent; it satisfies the Gibbs-Duhem Equation. Details on extending the models to other systems are in Appendix 10.7.

6.3 Pseudobinary Model

Boone et al. (1) developed an approach to correlate vapor-liquid equilibrium data for salt systems. This approach was applied to the $\text{Mg}(\text{NO}_3)_2$ - HNO_3 - H_2O system in the following manner.

Two pseudobinary components were defined, pure nitric acid and a pseudocomponent composed of the water and salt in the system. The influence of dissociation equilibria is not explicitly included. The effect of dissociation on vapor-liquid equilibrium is accounted for by the choice of reference-state fugacities for the pseudocomponents. The equilibrium criteria become:

Region of Predicted Curves

— — — Data exist

- - - - No Data Exist

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

VAPOR COMPOSITION AS A FUNCTION OF THE
LIQUID COMPOSITION — FULL-DISSOCIATION
MODEL

DATE
07/25/82

DRAWN BY
EHS

FILE NO.
CEPS-X-360

FIG.
12

— Within Range of Data
 - - - Extrapolation Out of Range of Data

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
 SCHOOL OF CHEMICAL ENGINEERING PRACTICE
 AT
 OAK RIDGE NATIONAL LABORATORY

PREDICTED BOILING TEMPERATURE AS A
 FUNCTION OF LIQUID COMPOSITION -
 FULL-DISSOCIATION MODEL

DATE
 07/25/82

DRAWN BY
 EHS

FILE NO.
 CEPS-X-360

FIG.
 13

$$Y_A^* = X_A \gamma_A P_A^0 \quad (63)$$

$$Y_{PB}^* = X_{PB} \gamma_{PB} P_{PB}^0 \quad (64)$$

where Y_{PB} is the vapor-phase, mole fraction of the pseudocomponent, which equals mole fraction of water vapor in the vapor phase because the salt is not volatile; X_{PB} is the liquid-phase mole fraction of the pseudocomponent ($X_{PB} = 1 - Y_A$); and γ_{PB} is the activity coefficients. The mole fraction of the pseudocomponent in the liquid phase X_{PB} is the sum of the mole fractions of water and salt in the liquid. The vapor pressure of the pseudocomponent is defined as the vapor pressure of water over a salt-water solution of the same composition as the pseudocomponent.

With this approach, the system can be examined as a binary system, and a suitable form for the activity coefficients can be chosen. The Wilson equation was used in this study to correlate the activity coefficients. The Wilson equation for this binary system is:

$$\ln \gamma_A = -\ln(X_A + \Lambda_{A-PB} X_{PB}) + X_{PB} \left[\frac{\Lambda_{A-PB}}{X_A + \Lambda_{A-PB} X_{PB}} - \frac{\Lambda_{PB-A}}{\Lambda_{PB-A} X_A + X_{PB}} \right] \quad (65)$$

$$\ln \gamma_{PB} = -\ln(X_{PB} + \Lambda_{PB-A} X_A) - X_A \left[\frac{\Lambda_{A-PB}}{X_A + \Lambda_{A-PB} X_{PB}} - \frac{\Lambda_{PB-A}}{\Lambda_{PB-A} X_A + X_{PB}} \right] \quad (66)$$

$$\Lambda_{i-j} = \frac{V_j^L}{V_i^L} \exp \left(\frac{-(\lambda_{ij} - \lambda_{ji})}{RT} \right) \quad (67)$$

$$\lambda_{ij} = \lambda_{ji} \quad (68)$$

where V_i^L and V_j^L refer to pure-component liquid molar volumes. Two parameters, λ_{ij} and λ_{ji} , are empirically fit.

The activity coefficients of the pseudobinary system were calculated from the ternary-system data. An Antoine equation was used to determine the vapor pressure of pure nitric acid, and the pseudocomponent vapor pressure was estimated with data from a binary $\text{H}_2\text{O}-\text{Mg}(\text{NO}_3)_2$ system. Details of these calculations are given in Appendix 10.4.

This approach was unsuccessful. The mean error involved in the ratio of the activity coefficients γ_A/γ_B was higher than 600%. The failure to accurately predict the vapor-liquid equilibrium for the $\text{Mg}(\text{NO}_3)_2-\text{HNO}_3-\text{H}_2\text{O}$ system was likely because of the inability of the model to characterize the complex dissociation equilibrium which exists between the nitric acid and the magnesium in solution.

6.4 Relative-Volatility Correlation

Johnson and Furter (10) determined an empirical correlation for the vapor-liquid equilibrium at their bubble points of ternary systems consisting of a salt, an alcohol, and water. Their correlation related relative volatility ϵ to the mole fraction of salt in the liquid phase X_S and was applied to the $\text{Mg}(\text{NO}_3)_2-\text{HNO}_3-\text{H}_2\text{O}$ system as follows:

$$\log \frac{\epsilon_{AW}}{\epsilon_{AW}^*} = kX_S \quad (69)$$

in which k is an empirically determined constant, subscripts A and W refer to nitric acid and water, respectively, and superscript * indicates a salt-free basis. The relative volatility of nitric acid with respect to water ϵ_{AW} is defined as:

$$\epsilon_{AW} = \frac{Y_A X_W}{X_A Y_W} \quad (70)$$

The relative volatility on a salt-free basis is:

$$\epsilon_{AW}^* = \frac{Y_A^* X_W^*}{X_A^* Y_W^*} \quad (71)$$

The salt-free, liquid-phase mole fractions are:

$$x_A^* = \frac{x_A}{x_A + x_W} \quad (72)$$

and

$$x_W^* = \frac{x_W}{x_A + x_W} \quad (73)$$

The vapor-phase mole fractions y_A^* and y_W^* were determined from the composition of the equilibrium vapor above a binary mixture whose composition is identical to the salt-free mole fractions. The correlation of Hala et al. (8) was used to determine the vapor-phase composition. For the $\text{HNO}_3\text{-H}_2\text{O}$ system, the correlation is:

$$\log \frac{y_A^*(1 - x_A^{*2})}{x_A^{*2}(1 - y_A^*)} = 2.5149 - 2.3211 x_A^{*1/2} - 2.1925(1 - 2x_A^*) \quad (74)$$

If the correlation of Johnson and Furter (10) for a ternary system of a salt and two nonelectrolyte solutes can be expanded to the $\text{Mg}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ system, in which one solute is an electrolyte, the following results:

$$\frac{\log \frac{\epsilon_{AW}}{\epsilon_{AW}^*}}{x_S} = \text{constant} \quad (75)$$

In Fig. 14, the term $[\log(\epsilon_{AW}/\epsilon_{AW}^*)/x_S]$ is plotted as a function of the liquid-phase mole fraction of acid x_A for the data of Shneerson et al. (19), Cigna et al. (2), and Ginnow and Clark (7). The data of Prosek (15) were omitted from this graph because the values for the ordinate were off-scale by a factor of 3 to 25 times the maximum ordinate value. No trend is observed in this graph which would permit correlation of the vapor-liquid equilibrium data. Additional calculations of the relative volatilities are in Appendix 10.5.

Weight Fraction HNO_3 in Liquid, Salt-Free Basis

DATA FROM:

Shneerson et al. (19)

Cigna et al. (2)

Ginnow and Clark (7)

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

RELATIVE VOLATILITY -- ATTEMPTED
CORRELATION

DATE
07/20/82

DRAWN BY
EHS

FILE NO.
CEPS-X-360

FIG.
14

7. CONCLUSIONS

1. Both the simplified dissociation model and the full-dissociation model correlate the entire range of existing vapor-liquid equilibrium data of the $\text{Mg}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ system. The average absolute deviations in predicted vapor-phase composition and bubble-point temperature were 8 mole % and 8 K, respectively, for the simplified dissociation model. Predicted azeotropic composition and temperature for the $\text{HNO}_3\text{-H}_2\text{O}$ system were 68 wt % HNO_3 and 393 K for this model. The full-dissociation model exhibited an average absolute deviation of 9 mole % for predicted vapor-phase composition, and 10 K for predicted bubble-point temperature. This model predicted an azeotrope for the $\text{HNO}_3\text{-H}_2\text{O}$ system at 63 wt % HNO_3 and 380 K. The major advantages of the models are an accurate estimation of the extent of dissociation for the simplified-dissociation model and thermodynamic consistency for the full-dissociation model.

2. The pseudobinary approach produced average errors of more than 600% for the ratio of the activity coefficients when correlated with a Wilson equation. Because of initial poor fit, further refinement of the model was not pursued.

3. The relative volatilities of HNO_3 and H_2O in the $\text{Mg}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ system could not be correlated to give accurate predictions of vapor-phase composition.

8. RECOMMENDATIONS

1. The simplified-dissociation model or the full-dissociation model should be refined to account for both extent of dissociation and thermodynamic consistency. This would lend confidence to their predictive capability and validate extrapolation to regions where experimental data do not exist.

2. More experimental data should be taken in the regions applicable to the two-pot process. These data should be used to test the validity of both the simplified-equilibrium model and the full-dissociation model.

3. The two successful correlations should be used to model the two-pot process.

9. ACKNOWLEDGMENTS

We thank our consultants, K. M. Counce, R. T. Jubin, and R. E. Barker for all their help. J. L. Marley's work on the experimental apparatus and P. W. Pair's work on the analyses were greatly appreciated.

10. APPENDIX

10.1 VLE Data

The vapor-liquid equilibrium data given in the literature sources (2, 7, 15, 19) and those obtained on the batch still are shown in the first four columns of Tables 1 to 6. The vapor concentrations and bubble-point temperature predicted by the simplified-dissociation model and the full-dissociation model are listed in these tables. The difference (residuals) between the predicted and experimental values of the HNO_3 vapor concentration and bubble-point temperature are given.

10.2 Simplified-Dissociation-Model Calculations

10.2.1 Calculation of Activity Coefficients

The extent of dissociation for the simplified-dissociation model is obtained from Eq. (30). The equilibrium constant is given by:

$$K = \exp (-\Delta G_R/RT) \quad (76)$$

This is expanded as:

$$\Delta G_R = \Delta H_R - T\Delta S_R \quad (77)$$

where ΔH_R and ΔS_R are the enthalpy and entropy changes of the reaction. The expression for ΔG_R from Eq. (77) is substituted into Eq. (76) to give:

$$K = [\exp (\frac{\Delta S}{R})][\exp(-\Delta H/RT)] \quad (78)$$

If the entropy and enthalpy changes do not depend on temperature, the equilibrium constant can be expressed as:

$$K = \bar{A} \exp (\frac{-\Delta H}{RT}) \quad (79)$$

Table 1. Vapor-liquid equilibrium data from Ginnow and Clark (7)

Experimental values				Simplified-dissociation model				Full-dissociation model			
Mg(NO ₃) ₂ in liquid (wt %)	HNO ₃ in liquid (wt %)	HNO ₃ in vapor (wt %)	Temp. (°C)	HNO ₃ in vapor (wt %)	Concentration residual (wt %)	Temp. (°C)	Temperature residual (°C)	HNO ₃ in vapor (wt %)	Concentration residual (wt %)	Temp. (°C)	Temperature residual (°C)
0.5980	0.0970	0.7340	140.0	0.8724	0.1384	136.840	-3.160	0.8936	0.1596	143.161	3.161
0.6015	0.0830	0.8450	140.0	0.8290	-0.0360	140.608	0.608	0.8566	-0.0084	147.630	7.630
0.5990	0.0855	0.8160	140.0	0.8319	0.0159	140.089	0.089	0.8587	0.0427	146.878	6.878
0.5990	0.0855	0.7690	145.0	0.8319	0.0629	140.130	-4.870	0.8587	0.0897	146.897	1.897
0.5985	0.0855	0.7930	141.0	0.8304	0.0374	140.176	-0.824	0.8573	0.0643	146.889	5.889
0.6155	0.0720	0.8690	141.0	0.8236	-0.0454	142.703	1.703	0.8548	-0.0142	151.249	10.249
0.6155	0.0715	0.9410	142.5	0.8212	-0.1198	142.848	0.348	0.8527	-0.0883	151.437	8.937
0.5990	0.1210	0.9260	135.0	0.9347	0.0087	128.041	-6.939	0.9460	0.0200	134.245	-0.755
0.6210	0.0920	0.8780	135.0	0.9106	0.0326	134.571	-0.429	0.9286	0.0506	142.922	7.922
0.5590	0.1735	0.9870	125.0	0.9578	-0.0392	119.460	-5.540	0.9627	-0.0243	122.808	-2.192
0.7070	0.0940	1.0170	137.0	0.9935	-0.0235	105.752	-31.248	0.9955	-0.0215	130.478	-6.522
0.6895	0.1150	0.4220	168.0	0.9949	0.5729	100.822	-67.178	0.9962	0.5742	123.530	-44.470
0.6560	0.0550	0.8620	150.0	0.8678	0.0058	145.127	-4.873	0.8997	0.0377	158.433	8.433
0.6515	0.0920	0.9530	138.0	0.9584	0.0054	126.586	-11.414	0.9687	0.0157	138.588	0.588
0.6825	0.0840	0.9780	140.0	0.9774	-0.0006	120.813	-19.187	0.9841	0.0061	137.959	-2.041
0.6375	0.1005	0.9490	136.0	0.9542	0.0052	126.495	-9.505	0.9646	0.0156	136.757	0.757
0.6675	0.0680	0.9580	144.0	0.9367	-0.0213	135.442	-8.558	0.9540	-0.0040	149.532	5.532
0.6375	0.1001	0.9520	137.0	0.9536	0.0016	126.691	-10.309	0.9641	0.0121	136.961	-0.039
0.6560	0.0525	0.7750	148.0	0.8558	0.0808	146.398	-1.602	0.8902	0.1152	159.870	11.870
0.6215	0.0715	0.8270	143.0	0.8403	0.0133	142.321	-0.679	0.8704	0.0434	151.394	8.394
0.6450	0.0300	0.6720	150.0	0.6273	-0.0447	155.311	5.311	0.6883	0.0163	169.971	19.971
0.6235	0.0950	0.9410	139.0	0.9228	-0.0182	132.754	-6.246	0.9387	-0.0023	141.348	2.348

Table 2. Vapor-liquid equilibrium data from Schneerson et al. (19)

Experimental values				Simplified-dissociation model				Full-dissociation model			
Mg(NO ₃) ₂ in liquid (wt %)	HNO ₃ in liquid (wt %)	HNO ₃ in vapor (wt %)	Temp. (°C)	HNO ₃ in vapor (wt %)	Concentration residual (wt %)	Temp. (°C)	Temperature residual (°C)	HNO ₃ in vapor (wt %)	Concentration residual (wt %)	Temp. (°C)	Temperature residual (°C)
0.0770	0.2050	0.0270	106.5	0.0385	0.0115	107.191	0.691	0.0254	-0.0016	103.349	-3.151
0.0780	0.2970	0.0840	110.5	0.0942	0.0102	110.500	0.000	0.0788	-0.0052	108.071	-5.429
0.0830	0.3990	0.2090	114.0	0.2300	0.0210	115.420	1.420	0.2304	0.0214	107.780	-6.250
0.0800	0.4910	0.4350		0.4293	-0.0057	119.741		0.4403	0.0253	109.327	
0.0770	0.5440	0.7410	120.8	0.4374	0.0146	122.249	1.449	0.4714	0.0404	108.835	-11.945
0.0800	0.5880	0.7410	121.0	0.7062	-0.0348	122.632	1.632	0.7473	0.0063	107.701	-13.099
0.0794	0.6890	0.9075		0.9168	0.0093	116.784		0.9321	0.0244	97.820	
0.0772	0.7540	0.9830	103.2	0.9738	-0.0092	106.894	3.494	0.9774	-0.0084	87.893	-15.307
0.2000	0.1700	0.0480	110.8	0.0785	0.0105	112.989	2.189	0.0591	-0.0089	108.714	-2.083
0.2030	0.2840	0.2270	116.3	0.2947	0.0277	119.146	2.846	0.2403	0.0133	112.530	-3.769
0.1980	0.3450	0.3980		0.3981	0.0181	122.011		0.3984	0.0184	113.834	
0.2040	0.3800	0.4990	121.2	0.5258	0.0268	124.097	2.897	0.5359	0.0349	114.460	-6.540
0.1970	0.4240	0.6350		0.6464	0.0114	124.868		0.6434	0.0284	113.714	
0.2040	0.4960	0.8310	121.2	0.8583	0.0273	122.271	1.071	0.8489	0.0379	108.581	-12.619
0.2050	0.5460	0.9140	114.5	0.9355	0.0215	115.849	1.349	0.9393	0.0253	101.463	-13.037
0.2020	0.5844	0.9830	108.0	0.9478	-0.0145	108.872	0.872	0.9491	-0.0139	94.831	-13.149
0.2970	0.0740	0.0410	111.0	0.0478	0.0068	115.007	4.007	0.0339	-0.0071	112.171	1.171
0.3000	0.1440	0.1400	115.6	0.1453	0.0053	119.268	3.668	0.1228	-0.0172	115.214	-0.384
0.2970	0.2220	0.3120	120.0	0.3302	0.0182	123.737	3.737	0.3144	0.0024	118.133	-1.847
0.2940	0.3220	0.4490	122.4	0.4933	0.0243	124.254	3.854	0.4897	0.0207	119.381	-3.019
0.3010	0.3170	0.6410	124.4	0.6495	0.0285	127.595	3.195	0.6744	0.0334	119.299	-5.101
0.2960	0.3680	0.7950	123.5	0.8120	0.0170	125.834	2.334	0.8179	0.0229	116.024	-7.474
0.3040	0.4150	0.9010	119.0	0.9189	0.0179	119.402	0.402	0.9204	0.0196	108.982	-10.018
0.3040	0.4850	0.9750	110.0	0.9809	0.0059	104.382	-5.618	0.9795	0.0045	95.494	-14.504
0.4020	0.0390	0.0670		0.0580	-0.0090	121.651		0.0473	-0.0197	120.208	
0.4050	0.0790	0.1810	116.8	0.1543	-0.0267	124.851	8.051	0.1378	-0.0432	122.934	4.134
0.4000	0.1290	0.3300	124.8	0.3105	-0.0195	127.851	1.051	0.2948	-0.0332	125.041	-1.759
0.4000	0.1880	0.5870	127.6	0.5548	-0.0322	130.774	3.174	0.5844	-0.0324	124.738	-0.845
0.4050	0.2090	0.6920	128.2	0.6603	-0.0317	131.195	2.995	0.6444	-0.0274	124.734	-1.464
0.4050	0.2280	0.7510	128.2	0.7315	-0.0195	130.447	2.447	0.7370	-0.0140	125.788	-2.448
0.3950	0.2930	0.8800	124.0	0.8838	0.0038	124.812	0.812	0.8849	0.0049	118.423	-5.577
0.4045	0.3440	0.9642	115.5	0.9642	0.0020	111.833	-3.667	0.9654	0.0014	104.583	-8.947
0.4975	0.0222	0.1303		0.0874	-0.0427	131.374		0.0842	-0.0461	132.903	
0.4923	0.0497	0.2848		0.2137	-0.0731	133.107		0.2115	-0.0753	134.243	
0.5007	0.0649	0.4379		0.3311	-0.1048	135.308		0.3389	-0.1020	136.415	
0.4916	0.1105	0.6265		0.5484	-0.0781	136.007		0.5905	-0.0640	136.208	
0.4985	0.1715	0.8583		0.8394	-0.0187	131.772		0.8508	-0.0075	130.907	
0.5115	0.2270	0.9448		0.9443	-0.0025	115.235		0.9444	-0.0004	115.658	
0.5930	0.0280	0.4607	145.4	0.4577	-0.0097	147.391	1.791	0.4748	-0.0354	156.428	10.318
0.6000	0.0445	0.6447	144.4	0.6440	-0.0807	147.795	3.195	0.6091	-0.0072	158.484	11.828
0.5995	0.0490	0.6540	144.0	0.6027	-0.0513	147.300	1.482	0.6448	-0.0125	152.678	9.178
0.5995	0.0644	0.7473	143.5	0.7219	-0.0254	144.982	1.482	0.7398	0.0128	150.484	8.984
0.5980	0.0730	0.7880	141.5	0.7671	-0.0209	143.299	1.799	0.8008	-0.0019	148.078	2.078
0.6000	0.0909	0.8820	138.0	0.8544	-0.0254	138.444	4.444	0.8801	-0.0091	145.539	7.939
0.6000	0.1044	0.8925	136.4	0.9052	-0.0127	133.249	-3.351	0.9214	0.0291	139.539	8.939
0.6000	0.1340	0.9420	119.5	0.9585	-0.0035	121.804	2.304	0.9455	0.0035	128.401	8.901

Table 3. Vapor-liquid equilibrium data from Cigne et al. (2)

Experimental values				Simplified-dissociation model				Full-dissociation model			
Mg(NO ₃) ₂ in liquid (wt %)	HNO ₃ in liquid (wt %)	HNO ₃ in vapor (wt %)	Temp. (°C)	HNO ₃ in vapor (wt %)	Concentration residual (wt %)	Temp. (°C)	Temperature residual (°C)	HNO ₃ in vapor (wt %)	Concentration residual (wt %)	Temp. (°C)	Temperature residual (°C)
0.1870	0.0720	0.0070	107.2	0.0167	0.0097	108.290	1.090	0.0091	0.0021	105.724	-1.476
0.1870	0.2150	0.0840	113.0	0.1142	0.0302	114.214	1.214	0.0934	0.0094	109.217	-3.783
0.1870	0.2810	0.1860	116.1	0.2154	0.0294	117.637	1.537	0.1992	0.0132	111.274	-4.826
0.1870	0.4160	0.5610	122.6	0.5790	0.0180	124.224	1.624	0.5953	0.0343	113.822	-8.778
0.1870	0.4820	0.7520	122.9	0.7740	0.0220	124.250	1.350	0.7913	0.0393	111.242	-11.658
0.2000	0.3300	0.3520	119.0	0.3618	0.0098	121.421	2.421	0.3583	0.0063	113.624	-5.376
0.2000	0.4710	0.7620	122.7	0.7857	0.0237	124.328	1.628	0.8008	0.0388	111.545	-11.155
0.3000	0.0000	0.0000	111.5	0.0000	0.0000	111.610	0.110	0.0000	0.0000	109.931	-1.549
0.3600	0.0000	0.0000	115.5	0.0000	0.0000	115.600	0.100	0.0000	0.0000	114.186	-1.314
0.3600	0.0580	0.0350	118.7	0.0630	0.0280	119.082	0.382	0.0491	0.0141	116.838	-1.842
0.3600	0.1340	0.2020	123.7	0.2269	0.0249	124.131	0.431	0.2079	0.0049	120.692	-3.008
0.3600	0.1840	0.3850	125.0	0.3945	0.0093	127.291	2.291	0.3529	-0.0021	122.842	-3.158
0.3600	0.2200	0.5390	126.7	0.5338	-0.0052	128.930	2.230	0.5309	-0.0081	123.441	-3.059
0.3600	0.2390	0.6150	127.4	0.6076	-0.0074	129.375	1.975	0.6084	-0.0066	123.604	-3.794
0.3600	0.3240	0.8410	125.3	0.8697	0.0287	124.845	-0.455	0.8729	0.0319	116.999	-8.301
0.3600	0.3880	0.9700	119.2	0.9611	-0.0089	112.629	-6.571	0.9403	-0.0097	109.091	-14.109
0.4500	0.0000	0.0000	125.0	0.0000	0.0000	123.664	-1.334	0.0000	0.0000	123.664	-1.334
0.4500	0.0320	0.0950	127.0	0.0764	-0.0181	128.212	-0.788	0.0683	-0.0247	125.915	-1.085
0.4500	0.1140	0.4820	129.7	0.4062	-0.0758	132.179	2.479	0.4041	-0.0779	130.825	1.125
0.4500	0.1550	0.6720	131.5	0.6038	-0.0682	133.418	1.918	0.6105	-0.0615	131.257	-0.243
0.4500	0.1770	0.7660	131.5	0.6997	-0.0663	133.016	1.516	0.7084	-0.0574	130.355	-1.145
0.4500	0.2400	0.8800	126.8	0.8927	0.0127	125.826	-0.974	0.8975	0.0175	122.042	-4.738
0.5250	0.0000	0.0000	133.5	0.0000	0.0000	133.378	-0.122	0.0000	0.0000	136.407	2.909
0.5250	0.0310	0.2610	136.2	0.3107	0.0497	137.590	1.390	0.3212	0.0602	140.365	4.165
0.5250	0.0910	0.5410	136.0	0.5750	0.0140	138.737	2.737	0.5956	0.0346	140.843	4.843
0.5250	0.1130	0.6290	134.6	0.7793	0.0685	137.816	3.216	0.7180	0.0890	139.382	4.782
0.5250	0.1340	0.7860	134.0	0.7793	-0.0167	135.940	1.940	0.7971	0.0011	137.132	3.132
0.5450	0.0000	0.0000	132.6	0.7990	-0.0700	135.279	2.679	0.8158	-0.0532	136.285	3.685
0.6000	0.0000	0.0000	136.5	0.0000	0.0000	136.573	0.073	0.0000	0.0000	140.951	4.451
0.6000	0.0280	0.1310	148.0	0.0000	0.0000	147.745	-0.255	0.0000	0.0000	157.524	9.524
0.6000	0.0670	0.3350	145.0	0.3867	0.2557	148.623	3.623	0.4285	0.2975	157.895	12.895
0.6000	0.1120	0.9400	143.5	0.7393	0.2043	144.524	1.024	0.7740	0.2410	152.148	8.648
0.6400	0.0000	0.0000	131.0	0.9182	-0.0218	131.245	0.245	0.9325	-0.0075	137.490	6.490
0.6830	0.0000	0.0000	158.5	0.0000	0.0000	158.651	0.151	0.0000	0.0000	175.142	16.642
			174.0	0.0000	0.0000	174.472	0.472	0.0000	0.0000	202.976	28.976

Table 4. Vapor-liquid equilibrium data from Prosek (15)

Experimental values				Simplified-dissociation model				Full-dissociation model			
Mg(NO ₃) ₂ in liquid (wt %)	HNO ₃ in liquid (wt %)	HNO ₃ in vapor (wt %)	Temp. (°C)	HNO ₃ in vapor (wt %)	Concentration residual (wt %)	Temp. (°C)	Temperature residual (°C)	HNO ₃ in vapor (wt %)	Concentration residual (wt %)	Temp. (°C)	Temperature residual (°C)
0.1332	0.0397	0.1327	120.7	0.0080	-0.1447	103.561	-13.139	0.0036	-0.1491	103.510	-17.102
0.1343	0.0587	0.1493	120.6	0.0077	-0.1418	103.505	-13.095	0.0035	-0.1460	103.481	-17.119
0.2473	0.0392	0.3091	121.6	0.0130	-0.2961	110.264	-11.336	0.0073	-0.3010	107.977	-13.623
0.2490	0.0393	0.3091	121.5	0.0132	-0.2959	110.356	-11.144	0.0075	-0.3016	108.060	-13.440
0.3300	0.0336	0.4655	121.1	0.0233	-0.4422	115.256	-5.844	0.0159	-0.4496	113.148	-7.952
0.3305	0.0332	0.4690	121.1	0.0231	-0.4459	115.271	-5.829	0.0157	-0.4533	113.172	-7.928
0.1711	0.0315	0.0980	116.5	0.0049	-0.0931	106.247	-10.253	0.0022	-0.0950	104.412	-12.000
0.1694	0.0301	0.0989	116.5	0.0046	-0.0943	106.130	-10.370	0.0020	-0.0969	104.330	-12.170
0.3765	0.0160	0.4790	120.2	0.0150	-0.4632	117.864	-2.336	0.0114	-0.4676	116.380	-3.820
0.3757	0.0158	0.4820	120.2	0.0154	-0.4666	117.786	-2.413	0.0111	-0.4709	116.296	-3.903
0.3220	0.0126	0.3070	120.3	0.0071	-0.2999	113.610	-6.689	0.0044	-0.3026	111.776	-8.524
0.3205	0.0121	0.3048	120.3	0.0067	-0.2981	113.486	-6.814	0.0042	-0.3006	111.653	-8.646

Table 5. Vapor-liquid equilibrium data from Marley (12)

Experimental values				Simplified-dissociation model				Full-dissociation model			
Mg(NO ₃) ₂ in liquid (wt %)	HNO ₃ in liquid (wt %)	HNO ₃ in vapor (wt %)	Temp. (°C)	HNO ₃ in vapor (wt %)	Concentration residual (wt %)	Temp. (°C)	Temperature residual (°C)	HNO ₃ in vapor (wt %)	Concentration residual (wt %)	Temp. (°C)	Temperature residual (°C)
0.5205	0.1013	0.5690	135.3	0.6165	0.0475	138.206	2.905	0.6365	0.0675	139.881	4.551
0.5720	0.0526	0.5330	140.0	0.5081	-0.0249	144.005	4.004	0.5424	0.0094	150.031	10.010
0.5778	0.0391	0.4540	145.0	0.4116	-0.0424	144.943	-0.057	0.4453	-0.0087	151.745	6.745
0.6048	0.0170	0.3994	150.0	0.2616	-0.1378	149.589	-0.410	0.2964	-0.1030	159.757	9.756
0.6198	0.0110	0.3000	155.0	0.2149	-0.0851	152.954	-2.046	0.2506	-0.0494	165.541	10.341
0.6458	0.0053	0.2036	160.0	0.1636	-0.0400	160.056	0.055	0.2011	-0.0025	177.421	17.421
0.6585	0.0003	0.1403	165.0	0.0129	-0.1274	164.783	-0.216	0.0169	-0.1234	185.605	20.605
0.5121	0.0989	0.5960	135.3	0.5677	-0.0283	137.631	2.331	0.5850	-0.0110	138.941	3.641
0.5461	0.0631	0.5400	140.0	0.4782	-0.0618	140.851	0.850	0.5028	-0.0372	144.781	4.780
0.5782	0.0444	0.4850	145.0	0.4634	-0.0216	145.000	0.000	0.4990	0.0140	151.697	6.697
0.6071	0.0273	0.3965	150.0	0.4090	0.0125	149.935	-0.065	0.4549	0.0584	160.032	10.031
0.6161	0.0240	0.3073	155.0	0.4058	0.0985	151.740	-3.259	0.4556	0.1483	163.075	8.075
0.6366	0.0066	0.2162	160.0	0.1728	-0.0434	157.395	-2.604	0.2086	-0.0076	172.763	12.762
0.6541	0.0044	0.1722	165.0	0.1583	-0.0139	162.736	-2.263	0.1976	0.0254	181.958	16.957
0.6826	0.0032	0.0658	175.0	0.1943	0.1285	172.903	-2.097	0.2519	0.1861	200.151	25.151

Table 6. Vapor-liquid equilibrium data from this study

Experimental values				Simplified-dissociation model				Full-dissociation model			
Mg(NO ₃) ₂ in liquid (wt %)	HNO ₃ in liquid (wt %)	HNO ₃ in vapor (wt %)	Temp. (°C)	HNO ₃ in vapor (wt %)	Concentration residual (wt %)	Temp. (°C)	Temperature residual (°C)	HNO ₃ in vapor (wt %)	Concentration residual (wt %)	Temp. (°C)	Temperature residual (°C)
0.3347	0.2893	0.7290	127.0	0.6965	-0.0325	128.502	1.502	0.7006	-0.0284	121.123	-5.876
0.4883	0.1265	0.6720	133.5	0.6192	-0.0528	135.757	2.257	0.6324	-0.0396	135.485	1.984
0.5509	0.0592	0.5780	140.5	0.4693	-0.1087	141.391	0.891	0.4952	-0.0828	145.716	5.216
0.6390	0.0309	0.4980	146.5	0.6083	0.1103	154.378	7.878	0.6679	0.1699	168.190	21.689
0.6069	0.0315	0.4140	151.5	0.4593	0.0453	149.679	-1.821	0.5067	0.0927	159.618	8.118
0.6400	0.0034	0.3040	156.5	0.0983	-0.2057	158.528	2.027	0.1213	-0.1827	174.800	18.300
0.6445	0.0030	0.2180	161.5	0.0942	-0.1238	159.900	-1.600	0.1174	-0.1006	177.138	15.638
0.6544	0.0046	0.1430	166.5	0.1656	0.0226	162.829	-3.671	0.2064	0.0634	182.068	15.568
0.6819	-0.0023	0.0780	172.5	-0.1810	-0.2590	174.927	2.427	-0.2692	-0.3472	203.767	31.267

where the constant $\bar{A}$ is given by:

$$\bar{A} = \exp(\Delta S/R) \quad (80)$$

The value of ΔH at 298 K was given by Young et al. (22) as 2900 cal/mol so that:

$$\frac{\Delta H}{R} = \frac{2900 \text{ cal/mol}}{1.987 \text{ cal/mol K}} = 1459 \text{ K}$$

The equilibrium constant in terms of mole fraction is given by Davis (4) as 0.2 at 298 K. The value of $\bar{A}$ is determined by rearranging Eq. (79):

$$\bar{A} = 0.2 e^{-1459 \text{ K}/298.3 \text{ K}} = 0.0015$$

The equilibrium is then given by:

$$K = 0.0015 e^{1459/T} \quad (81)$$

The extent of dissociation is from Eq. (37) rearranged to give:

$$(1 + K) X_A \alpha^2 + [2X_S (1 + K) - KX_A + K] \alpha + (-K - 2KX_S) = 0 \quad (82)$$

For the values of Schneerson et al. (19), $X_A = 0.0745$, $X_S = 0.0119$, $T = 379.5 \text{ K}$ and $Y_A = 0.0079$. The equilibrium constant is given by Eq. (81) which yields $K(379.5 \text{ K}) = 0.07$. The extent of dissociation is given by rearranging Eq. (37):

$$(1 + K) X_A \alpha^2 + [2X_S (1 + K) - KX_A + K] \alpha + (-K - 2KX_S) = 0 \quad (83)$$

In this case:

$$\begin{aligned} (1 + 0.0701)(0.0745)\alpha^2 + [2(0.0119)(1 + 0.0701) - (0.0701)(0.0745) \\ + 0.0701]\alpha + [-0.0701 - 2(0.0701)(0.0119)] = 0 \end{aligned}$$

The solution is:

$$\alpha = 0.538$$

After the extent of dissociation is determined the total species mole fractions are calculated from Eqs. (35) and (36). In this case:

$$x_A = \frac{(1 - 0.538)(0.0745)}{[1 + 0.538(0.0745) + 2(0.0019)]} = 0.0323$$

and

$$x_W = \frac{0.538[1 - 0.0745 - 0.0119]}{[1 + 0.538(0.0745) + 2(0.0119)]} = 0.8587$$

The vapor pressures of HNO_3 and H_2O are given by Antoine equations:

$$\log_{10} p_W^0(\text{torr}) = 7.949 - \frac{1657.4}{T(^{\circ}\text{C}) + 227.1} \quad (13) \quad (84)$$

$$\log_{10} p_A^0(\text{torr}) = 7.616 - \frac{1486.2}{T(^{\circ}\text{C}) + 230} \quad (5) \quad (85)$$

The vapor pressure for the acid at 372.8 K is given by:

$$\begin{aligned} \log_{10} p_A^0(\text{torr}) &= 7.616 - \frac{1486.2}{T(^{\circ}\text{C}) + 230} \\ &= 3.199 \end{aligned}$$

$$p_A^0 = 1583 \text{ torr} = 0.21 \text{ MPa}$$

and similarly the water vapor pressure is:

$$p_W^0 = 957 \text{ torr} = 0.13 \text{ MPa}$$

The activity coefficients are given by:

$$\gamma_i' = \frac{y_i \pi}{x_i' p_i^0} \quad (86)$$

For the acid:

$$\gamma_A' = \frac{(0.0079)(0.101 \text{ MPa})}{(0.0323)(0.21 \text{ MPa})} = 0.117$$

Similarly, the water activity coefficient is:

$$\gamma_W' = 0.917$$

10.2.2 Correlation of Activity Coefficients

The activity coefficients for water and nitric acid were calculated for the data of Potier (14) as in Appendix 10.2.1. The activity coefficient for pure HNO_3 was 1.82 at its normal boiling point. The correlations were:

$$[\ln \gamma_{\text{HNO}_3} - \ln 1.82] = -A_{\text{HNO}_3,1}(1 - x_A) - A_{\text{HNO}_3,2}(1 - x_A^2) \quad (87)$$

$$\ln \gamma_{\text{H}_2\text{O}} = A_{\text{H}_2\text{O},1} x_A + A_{\text{H}_2\text{O},2} x_A^2 \quad (88)$$

These were linearized as:

$$\frac{\ln \gamma_{\text{HNO}_3} - 0.60}{(1 - x_A)} = -A_{\text{HNO}_3,1} - A_{\text{HNO}_3,2} (1 + x_A) \quad (89)$$

$$\frac{\ln \gamma_{\text{H}_2\text{O}}}{x_A} = A_{\text{H}_2\text{O},1} + A_{\text{H}_2\text{O},2} x_A \quad (90)$$

The coefficients were found from a least-squares regression of Eqs. (89) and (90) as:

$$\ln \gamma_{\text{HNO}_3} = -2.52 + 6.210 x_A - 3.10 x_A^2 \quad (91)$$

$$\ln \gamma_{\text{H}_2\text{O}} = -0.17 x_A - 3.620 x_A^2 \quad (92)$$

The average absolute difference in x_i between the $\ln \gamma_i$ correlation and the experimental values was 0.06 mol fraction for the HNO_3 and 0.04 mol fraction for the H_2O .

The activity coefficients for the water in the $\text{Mg}(\text{NO}_3)_2\text{-H}_2\text{O}$ system with $\text{Mg}(\text{NO}_3)_2$ concentration up to .8 wt % were similarly correlated and were found best to be fit by:

$$\ln \gamma_w' = -4.47 x_S - 15.38 x_S^2 \quad (93)$$

The average absolute residual of $\ln \gamma$ was 0.01.

The ternary-mixture data of Shneerson et al. (19) and Cigna et al. (2) were used to fit the four remaining parameters. The regression was a least-squares fit of the error of:

$$\begin{aligned} \ln \gamma_{\text{HNO}_3} + 2.52 - 6.210 x_A + 3.10 x_A^2 = & A_{\text{HNO}_3,3} x_S + A_{\text{HNO}_3,4} x_S^2 \\ & - A_{\text{HNO}_3,5} (1 - x_A) x_S \end{aligned} \quad (94)$$

The correlation obtained was:

$$\begin{aligned} \ln \gamma_{\text{HNO}_3} = & -2.52 + 6.21 x_A - 3.10 x_A^2 + 23.83 x_S - 24.20 x_S^2 \\ & - 15.8 x_A x_S \end{aligned} \quad (95)$$

The water activity coefficients were similarly correlated by:

$$\ln \gamma_{H_2O} = -0.17 x_A - 3.62 x_A^2 - 4.47 x_S - 15.38 x_S^2 - 28.20 x_A x_S \quad (96)$$

The root-mean-square error in this correlation was 0.074 for $\ln \gamma_{HNO_3}$ and 0.02 for $\ln \gamma_{H_2O}$.

10.3 Full-Dissociation-Model Calculations

10.3.1 Calculation of Activity Coefficients

The mean rational activity coefficients for nitric acid and water are calculated from the ternary data by rearranging Eqs. (54) and (55):

$$\gamma_{\pm}^2 = \frac{Y_A \pi}{4 x_{\pm}^2 P_W^0} \quad (97)$$

$$\gamma_W' = \frac{Y_W \pi}{x_W' P_W^0} \quad (98)$$

The values of Y_A and Y_W are obtained directly from the ternary-mixture VLE data; $x_{\pm}$ and x_W' are calculated from the liquid-phase composition; and vapor pressures P_A^0 and P_W^0 are calculated from the Antoine equations for the pure liquids. A sample calculation follows. For the first value given by Schneerson et al. (19):

mole fractions of liquid phase:

$$x_S = 0.0119$$

$$x_A = 0.0745$$

$$x_W = 0.9136$$

mole fractions of vapor phase:

$$Y_A = 0.0079$$

$$Y_W = 0.9921$$

temperature:

$$T = 379.5 \text{ K } (106.5^\circ\text{C})$$

The following quantities are calculated from Eq. (52):

$$x_{\pm}^2 = \frac{0.0745[0.0745 + 2(0.0019)]}{[1 + 0.0745 + 2(0.0119)]^2} = 0.00607$$

From Eq. (55):

$$x_w^{\pm} = \frac{0.9136}{1 + 0.0745 + 2(0.0119)} = 0.832$$

From the Antoine equations:

$$\begin{aligned} \log_{10} p_A^0 (\text{torr}) &= 7.616 - \frac{1486.2}{T(^{\circ}\text{C}) + 230} \\ &= 7.616 - \frac{1486.2}{106.5 + 230} \end{aligned}$$

$$p_A^0 = 1583 \text{ torr} = 0.21 \text{ MPa}$$

$$\begin{aligned} \log_{10} p_W^0 &= 7.949 - \frac{1657.4}{T(^{\circ}\text{C}) + 227.1} \\ &= 7.949 - \frac{1657.4}{106.5 + 227.1} \end{aligned}$$

$$p_W^0 = 957 \text{ torr} = 0.13 \text{ MPa}$$

At one atmosphere $\pi = 0.101$ MPa (760 torr). From Eqs. (97) and (98):

$$\gamma_{\pm}^2 = \frac{0.0079 (1.101 \text{ MPa})}{4(0.00607)(0.21 \text{ MPa})} = 0.156$$

$$\gamma_w' = \frac{0.9921 (1.101 \text{ MPa})}{0.832(0.21 \text{ MPa})} = 0.947$$

10.3.2 Correlation of Activity Coefficients

The data of Schneerson et al. (19) and Cigna et al. (2) were used to fit the constants of Eqs. (59) and (60). Two observations by Cigna et al. were not used in the correlation because they were inconsistent with the remainder of the data.

The logarithm of the ratio of the activity coefficients is given by:

$$\begin{aligned} \ln (\gamma_{\pm}^2 / \gamma_w') &= B_1 + 3/2 c I^{1/2} + 2dI + (B_{SA} - B_{SW}) X_S \\ &+ B_{AW} (X_w - X_A) \end{aligned} \quad (99)$$

The terms of this expression are not linearly independent so that the values of all the constants cannot be obtained by a single linear regression. It is, however, desirable to minimize the error of $\ln (\gamma_{\pm}^2 / \gamma_w')$ because the ratio of the two activity coefficients is important in determining vapor-phase composition.

First, linear regressions of $\ln (\gamma_{\pm}^2 / \gamma_w')$ were performed with the three possible combinations of $I^{1/2}$ and two of the mole fractions X_A , X_w , and X_S . These regressions determined the value of c and set constraints on the values of the remaining five parameters. The values of c determined was then used in the individual activity coefficient equations as:

$$\begin{aligned} \ln \gamma_{\pm}^2 - c(3/2 I^{1/2} - 1/2 I^{3/2}) &= B_1 + d(2I - I^2) \\ &+ B_{AW} X_w + B_{SW} X_S \end{aligned} \quad (100)$$

$$\ln \gamma_w' + 1/2 c I^{3/2} = -dI^2 + B_{AW} X_A + B_{SW} X_S \quad (101)$$

The left-hand side of each equation was regressed against the right-hand side, and an average value of d was calculated from the results. (The values of d obtained from each regression differed by less than 2.5%.) The values of c and d were then used with the constraints from the regression of $\ln(\gamma_{\pm}^2/\gamma_W^2)$ to find values for B_{AW} and the difference $B_{AS} - B_{SW}$.

Finally, Eqs. (100) and (101) were rearranged to isolate two unknown parameters, B_{AS} and B_{SW} . The remaining terms were regressed for both equations to yield values for B_{AS} and B_{SW} . The difference between these two values ($B_{AS} - B_{SW}$) was within 1% of that value determined by the original constraints of the $\ln(\gamma_{\pm}^2/\gamma_W^2)$ regressions.

10.4 Calculations for the Pseudobinary Model

From the ternary-mixture data, the activity coefficients for the pseudobinary components were calculated. Rearrangement of Eq. (18) gives:

$$\gamma_A = \frac{Y_A \pi}{X_A P_A^0} \quad (102)$$

and

$$\gamma_{PB} = \frac{Y_{PB} \pi}{X_{PB} P_{PB}^0} \quad (103)$$

Substitution of the relations $Y_{PB} = 1 - Y_A$ and $X_{PB} = 1 - X_A$ into Eq. (103) and rearranging gives:

$$\gamma_{PB} = \frac{(1 - Y_A) P}{(1 - X_A) P_{PB}^0} \quad (104)$$

The mole fraction X_A and Y_A were obtained directly from the vapor-liquid equilibrium data and P_A^0 is determined by an Antoine equation for nitric acid [see Eq. (40)]. P_{PB}^0 was estimated with $\text{Mg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. It was assumed that:

$$P_{PB}^0 = f(X_S) - P_W^0 \quad (105)$$

where f is a function of only the amount of salt present in a binary salt-water mixture, and P_W^0 is the vapor pressure of pure water. P_W^0 was calculated from an Antoine equation [see Eq. (39)] and $f(X_S)$ was fitted to available binary-mixture data. The data were well fit by the function:

$$f = 10^{-6.128X^2 - 3.265X} \quad (106)$$

The activity coefficients were calculated from the literature data. A nonlinear regression was performed for Eqs. (65) and (66) with the Cigna and Schneerson data. The liquid molar volumes for the components which appear in the Λ terms were calculated from density data. For the pure acid:

$$V^L = \frac{63.01}{1.0521 - 0.00182 T} \quad (107)$$

where V^L is volume, ml/mole. This equation utilizes an expression for the density of pure HNO_3 presented by Stern and Kay (21). For the pseudocomponent of water and magnesium nitrate, density data for the binary system (16) was used to estimate a functional dependence of:

$$V_{PB}^L = \left[\left(\frac{W_S}{148.3} + \frac{1 - W_S}{18} \right) (0.7888 + 1.354 W_S - 0.000762 T) \right]^{-1} \quad (108)$$

where W_S is the weight fraction of the salt in the salt-water pseudocomponent. The units of V_{PB} are ml/mole, and T is expressed in K.

The fit of the data was poor (greater than 600% average error in γ_A/γ_{PB}), so further refinement of the model was not attempted.

10.5 Relative Volatility Calculations

The following relative-volatility calculation was typical for the data points of Cigna et al. (2). The data, in mole fraction, is:

$$X_A = 0.08408$$

$$X_S = 0.14315$$

The definition of the relative volatility of nitric acid with respect to water is:

$$\epsilon_{AW} = \frac{Y_A X_W}{X_A Y_W} \quad (70)$$

The liquid-phase mole fraction of water is expressed in terms of the acid and salt mole fractions as:

$$X_W = 1 - X_A - X_S \quad (109)$$

The vapor-phase mole fraction of water is expressed in terms of the acid mole fraction as:

$$Y_W = 1 - Y_A \quad (110)$$

because there is no salt in the vapor. Substitution for X_W and Y_W in Eq. (70) yields:

$$\epsilon_{AW} = \frac{Y_A (1 - X_A - X_S)}{X_A (1 - Y_A)} \quad (111)$$

This is evaluated from the experimental data to give:

$$\epsilon_{AW} = \frac{(0.52715)(1 - 0.08408 - 0.14315)}{(0.08408)(1 - 0.52715)}$$

$$\epsilon_{AW} = 10.2463$$

Equations (72), (73), and (109) are combined to express the salt-free liquid mole fractions as:

$$X_A^* = \frac{X_A}{1 - X_S} \quad (112)$$

and

$$x_w^* = \frac{(1 - x_A - x_S)}{1 - x_S} \quad (113)$$

The vapor mole fraction of acid y_A^* is correlated by H $\acute{a}$ la et al. (9) as:

$$\log \frac{y_A^* (1 - x_A^{*2})}{x_A^{*2} (1 - y_A^*)} = 2.5149 - 2.3211 x_A^{*1/2} - 2.1925 (1 - 2x_A^*) \quad (114)$$

This equation is rearranged to express y_A^* explicitly as:

$$y_A^* = \frac{n}{1 + n} \quad (115)$$

where

$$n = \frac{10^\psi x_A^{*2}}{1 - x_A^{*2}} \quad (116)$$

and

$$\psi = 2.5149 - 2.3211 x_A^{*1/2} - 2.1925(1 - 2x_A^*) \quad (117)$$

From Eq. (109), x_A^* is:

$$x_A^* = \frac{0.08408}{1 - 0.14315} = 0.09813$$

Substitution of this value into the expression for ψ gives:

$$\psi = 2.5149 - 2.3211(0.09813)^{1/2} - 2.1925[1 - 2(0.09813)]$$

$$\psi = 0.02560$$

Substitution for ψ and X_A^* into Eq. (116) yields:

$$\eta = \frac{10^{0.02560} (0.09813)^2}{1 - (0.09813)^2} = 0.01031$$

This result is used to evaluate Y_A^* from Eq. (112):

$$Y_A^* = \frac{0.01031}{1.01031} = 0.01020$$

The salt-free relative volatility is expressed in terms of the liquid and vapor acid mole fractions as:

$$\epsilon_{AW}^* = \frac{Y_A^* (1 - X_A^*)}{X_A^* (1 - Y_A^*)} \quad (118)$$

Substitution of $X_A^* = 0.09813$ and $Y_A^* = 0.01020$ into the above equation yields:

$$\epsilon_{AW}^* = \frac{0.01020 (1 - 0.09813)}{0.09813 (1 - 0.01020)} = 0.09279$$

The logarithm of the relative-volatility ratio becomes:

$$\log \frac{\epsilon_{AW}}{\epsilon_{AW}^*} = \log \frac{(10.2463)}{(0.09279)} = 2.043$$

10.6 Bubble-Point Program

Two computer programs to calculate the vapor composition and bubble-point temperature for a given liquid composition and pressure were written for the simplified-dissociation model and the full-dissociation model. The programs were used to predict the values of vapor composition and temperature for the experimental data points given in Appendix 10.1.

The programs were quite similar, and a flow chart is given in Fig. 15. The equations for the two models are given in Sects. 6.1 and 6.2. The calculation proceeds by first guessing a temperature. The equilibrium constant and vapor pressure are calculated from the temperature. The extent of dissociation and the total species mole fraction are estimated from the equilibrium constant and the analytical mole fractions. The activity coefficients are calculated from the correlations. The partial pressure, vapor composition, and total pressure are calculated. The total pressure is compared with the actual system pressure and, if necessary, the temperature is changed. The secant method is used to guess the next temperature from the previous two temperature iterations (13).

10.7 Model Extension

Both the simplified dissociation model and the full-dissociation model can be generalized to multicomponent electrolyte systems. Each model uses only binary interaction parameters so that many parameters can be fit from binary vapor-liquid equilibrium (VLE) data. The following general approaches can be taken.

For the simplified dissociation model, any number of extents of dissociation can be defined along with a corresponding simplified equilibrium Eq. (32).

In general, a polynomial in terms of the extents of dissociation must be solved for each equilibrium equation to obtain an estimate of dissociation. After total-species mole fractions are calculated from the analytical mole fractions and extents of dissociation, the activity coefficients can be calculated for each species.

These activity coefficients can then be correlated in the form:

$$\ln \gamma_i = A_{0i} + \sum_{j=1}^{N-1} A_{ji} X_j + \frac{1}{2} \sum_{k=1}^{N-1} \sum_{j=1}^{N-1} B_{kj} X_k X_j \quad (119)$$

where the undissociated solvent mole fraction is excluded from the above expansions and $B_{kj} = B_{jk}$. Equation (17) is then used to predict VLE.

For the full-dissociation model, the ionic contribution to excess Gibbs energy G^A does not change. The molecular contribution to excess Gibbs energy G^B has the form:

$$G^B = \sum_{i=1}^N B_i X_i + \frac{1}{2} \sum_{j=1}^N \sum_{k=1}^N B_{jk} X_j X_k \quad (120)$$

where

$$B_{\text{solvent}} = 0 \quad (121)$$

$$B_{jk} = B_{kj} \quad (122)$$

$$B_{jj} = 0 \quad (123)$$

If the total excess Gibbs energy is then differentiated with respect to mole number at constant temperature and pressure, expressions for the mean rational ionic activity coefficients are obtained which can be correlated. The definitions for mean ionic molarities and mean ionic activity coefficients are:

$$X_{i\pm} = (X_{i+}^{\nu_{i+}} X_{i-}^{\nu_{i-}})^{1/(\nu_{i+} + \nu_{i-})} \quad (124)$$

$$\gamma_{i\pm} = (\gamma_{i+}^{\nu_{i+}} \gamma_{i-}^{\nu_{i-}})^{1/(\nu_{i+} + \nu_{i-})} \quad (125)$$

10.8 Location of Data

Data for the batch-still experiments are located in ORNL Databook A-9909-G, pp. 79-89. The databook and calculations are on file with the MIT School of Chemical Engineering Practice, Bldg. 1505, ORNL.

10.9 Nomenclature

a	Activity
A^-	Anion
$A_{i1(2,3\dots)}$	Constants for $\ln \gamma_i$ correlation
$\bar{A}$	Pre-exponential term in equilibrium-constant expression
b, c, d	Constants for coulombic term of excess Gibbs energy
B_{ij}	Constants for noncoulombic term of excess Gibbs energy
f	Fugacity, Pa
G	Gibbs energy, J
G^A	Gibbs energy for coulombic interactions, J
G^B	Gibbs energy for noncoulombic interactions, J
ΔH	Heat of reaction J/mole
I	Ionic strength
k	Constant in relative-volatility correlation
K	Equilibrium constant
M^+	Cation
MA	Molecular electrolyte
n	Moles
N	Total moles; number of different species
N_R	Number of species involved in a reaction
P	Pressure, Pa
R	Gas constant, J/mol K
ΔS	Entropy of reaction J/K mol
T	Temperature, K
V	Liquid molar volume, ml/mole

W_S	Weight fraction of magnesium nitrate in pseudobinary component
X	Liquid-phase mole fraction
Y	Vapor-phase mole fraction
Z_i	Charge on ionic species i

Greek Symbols

α	Extent of dissociation
β_{12}	Separation factor
γ	Activity coefficients
Λ	Wilson parameter
μ	Chemical potential, J/mol
ν	Stoichiometric coefficient
π	Total pressure, Pa
ϕ	Fugacity coefficient
ψ	Function used in relative-volatility correlation
η	Function used in relative-volatility correlation
ϵ_{ij}	Relative volatility of i with respect to j
λ_{ij}	Empirical parameters of Wilson equation

Subscripts

A	Acid
H^+	Hydrogen ion
HNO_3	Nitric acid
i	Species i
MA	Undissociated electrolyte
NO_3^-	Nitrate ion
0	Reference pressure

PB	Pseudobinary
R	Reaction
S	Salt
W	Water
+	Cation
-	Anion
$\pm$	Mean ionic

Superscripts

E	Excess energy
L	Liquid
V	Vapor
$\wedge$	Mixture
o	Reference state or vapor pressure
*	Salt-free basis
I	Actual composition of total species

10.10 References

1. Boone, J. E., R. W. Rousseau, and E. M. Schoenborn, "The Correlation of Vapor-Liquid Equilibrium Data for Salt-Containing Systems," in Thermodynamic Behavior of Electrolytes in Mixed Solvents, W. F. Furter, ed., American Chemical Society, Washington, D.C., 1976.
2. Cigna, R., S. DiCave, A. R. Giona, and E. Mariani, "Effect of Alkali and Alkali-Earth Nitrates on the Liquid-Vapor Equilibrium of the Water Nitric Acid System," La Chimica e L'Industria, 46(1), 36 (1964).
3. Counce, R. M., W. S. Groenier, T. L. Hebble, W. D. Holland, R. T. Jubin, E. D. North, and L. E. Thompson, Jr., "The Extractive Distillation of Nitric Acid Using the Two-Pot Concept," ORNL/TM-7982, December 1982.

4. Davis, W., Jr. and H. J. deBruin, "New Activity Coefficients of 0-100 Percent Aqueous Nitric Acid," J. Inorg. Nucl. Chem. (26) pp. 1069-1083, 1964.
5. Denbigh, K., The Principles of Chemical Equilibrium, 3rd ed., Cambridge University Press, 1971.
6. Duisman, J. A. and S. A. Stern, "Vapor Pressure and Boiling Point of Pure Nitric Acid," J. of Chem. and Eng. Data, 14(4), 457 (1969).
7. Girnow, R. J. and W. E. Clark (Oak Ridge National Laboratory), "Iodex Recycle Studies, Scoping Studies of the Solubility of Iodix Acid and of Vapor-Liquid Equilibria in the System: 60 to 80% $\text{Mg}(\text{NO}_3)_2$ - 0 to 20% HNO_3 - 20 to 40% H_2O ," internal document (December 1978).
8. Hála, E., I. Wichterle, J. Polák, and T. Boublik, Vapor-Liquid Equilibrium Data at Normal Pressures, Pergamon, New York, 1968.
9. Hála, E., J. Pick, V. Fried, and O. Vilim, Vapor-Liquid Equilibrium, 2nd English Edition, Pergamon Press, New York, 1967.
10. Johnson, A. I. and W. F. Furter, "Salt Effect in Vapor-Liquid Equilibrium, Part II," Canadian J. Chem. Eng. Volume 6, pp. 78-86, 1960.
11. Lewis, G. N., M. Randall, K. S. Pitzer, and L. Brewer, Thermodynamics, 2nd ed., McGraw-Hill, New York, 1961.
12. Marley, J. L., Personal communication, ORNL, July 19, 1982.
13. Perry, J. H., ed., Chemical Engineers' Handbook, 4th ed., McGraw-Hill, New York, 1963.
14. Potier, J., "Étude des Propriétés Thermodynamiques de Systems," Sciences Physiques 4, 99 (1958).
15. Prosek J., Ph.D. Thesis, Utzcht-Csan, Prague, 1965.
16. Rainer, R. H. (Oak Ridge National Laboratory), "The Densities of Magnesium Nitrate Salts from Their Melting Temperatures to 240°C," internal document (1975).
17. Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, The Properties of Gases and Liquids, 3rd edition, McGraw-Hill, New York, 1977.
18. Robinson, R. A. and R. H. Stokes, Electrolyte Solutions, 2nd ed., Butterworth, London, 1959 (reprinted 1965).
19. Shneerson, A. L., M. A. Miniovich, Zh. M. Filippova, S. N. Soroka, and P. A. Platonov, "Liquid-Vapor Equilibria in the Systems Nitric Acid-Water-Magnesium Nitrate, Nitric Acid-Water-Calcium Nitrate, and Nitric Acid-Water-Magnesium Nitrate-Calcium Nitrate," Russian J. Phys. Chem. 39(6), pp. 744-747, 1965.

20. Smith, J. M. and H. C. VanNess, Introduction to Chemical Engineering Thermodynamics, 2nd ed., McGraw-Hill, New York, 1959.

21. Stern, S. A. and W. B. Kay, "The Orthobaric Density of Pure Nitric Acid," J. Am. Chem. Soc. 76, 5353 (1954).

22. Young, T. F., L. F. Maranville, and H. M. Smith, "Raman Spectral Investigations of Ionic Equilibria in Strong Electrolytes," The Structure of Electrolyte Solutions, Chpt. 4, W. J. Hamer, ed., Wiley, New York, 1959.

ABSTRACT

The vapor-liquid equilibrium of the $\text{Mg}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ system in concentrations of 0 to 70 wt % $\text{Mg}(\text{NO}_3)_2$ and 0 to 75 wt % HNO_3 at atmospheric pressure was correlated by two approaches. One was based on a dissociation equilibrium expression in which the activities of the reacting species (HNO_3 , NO_3^- , and H^+) were approximated with mole fractions. The activity coefficients of the undissociated HNO_3 and H_2O were correlated as functions of the concentrations of magnesium nitrate and nitric acid by second-order polynomials. The average absolute difference between predicted and experimental values was 8% for the mole fraction of acid in the vapor and 8 K for the bubble-point temperature. The second approach was to correlate the mean ionic rational activity coefficient of water with a form of the excess Gibbs energy composed of two terms. One term, a function of the ionic strength, accounts for the coulombic (ionic) interactions; the other term accounts for the non-coulombic (molecular) interactions. The average absolute difference between predicted and experimental values was 9% for the mole fraction of acid in the vapor, and 10 K for the bubble-point temperature.

INTERNAL DISTRIBUTION

1-2.	R. E. Barker	17.	E. D. North
3.	W. D. Burch	18.	R. H. Rainey
4.	J. H. Clinton	19.	C. D. Scott
5.	H. D. Cochran, Jr.	20.	J. S. Watson
6.	D. A. Costanzo	21.	J. E. Wortman
7-8.	R. M. Counce	22.	R. G. Wymer
9.	W. S. Groenier	23.	O. O. Yarbrow
10.	J. R. Hightower, Jr.	24-25.	Central Research Library
11-12.	R. T. Jubin	26.	Document Reference Section
13.	B. E. Lewis	27-29.	Laboratory Records
14.	J. L. Marley	30.	Laboratory Records, ORNL R.C.
15.	G. E. Moore	31.	ORNL Patent Office
16.	E. L. Nicholson		

EXTERNAL DISTRIBUTION

- 32-48. MIT Practice School, GA, Selkirk, NY 21258
- 49. W. C. Rousseau, MIT, Cambridge, MA 02139
- 50. Irvin Higgins, Chem. Seps. Corp., 1 Tech. Park, Knoxville, TN 37922
- 51. J. W. Tester, MIT, Cambridge, MA 02139
- 52. J. E. Vivian, MIT, Cambridge, MA 02139
- 53. Morgantown Energy Technology Center, P.O. Box 880, Morgantown, WV 25405
- 54. Office Asst. Mgr., Energy R&D, DOE, Oak Ridge, TN 37830
- 55-82. Technical Information Center