



Computer calculations for binary electrolyte vapor-liquid equilibrium  
by Gary Dale Nelson

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of  
MASTER OF SCIENCE in Chemical Engineering  
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**Abstract:**

An investigation has been made into vapor-liquid equilibrium for binary monovalent electrolyte systems. These electrolyte systems were treated as systems which deviate from nonelectrolyte behavior due to their dissociation in the liquid phase. Corrections to this nonelectrolyte behavior were made in fitting programs written to predict phase equilibrium for nonelectrolytes .

Improvements were made in the fitting programs for hydrochloric acid by considering the mole fraction of undissociated electrolyte molecules in the liquid phase as the liquid phase solute concentration. This undissociated molecule concentration was obtained from a concentration dependent dissociation curve.

Slightly dissociating electrolytes such as ammonia seem to differ much less from nonelectrolyte behavior than do highly dissociating electrolytes such as hydrochloric and hydrobromic acid.

COMPUTER CALCULATIONS FOR BINARY  
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## TABLE OF CONTENTS

Chapter		Page
	VITA . . . . .	ii
	ACKNOWLEDGMENT . . . . .	iii
	LIST OF TABLES . . . . .	v
	LIST OF FIGURES . . . . .	vi
	ABSTRACT . . . . .	vii
I	INTRODUCTION . . . . .	1
	Nonelectrolyte Vapor-Liquid Equilibrium . . . . .	2
	Characteristics of Electrolyte Solutions . . . . .	8
II	STATEMENT OF THE PROBLEM . . . . .	20
III	PROCEDURE . . . . .	22
	Undissociated Liquid Phase Molecules . . . . .	24
	Excess Gibbs Energy . . . . .	25
IV	RESULTS . . . . .	29
V	SUMMARY . . . . .	43
	APPENDIX . . . . .	45
	Appendix A: Derivations of Corrections to Programs . . . . .	46
	Appendix B: Listing of Programs . . . . .	54
	Appendix C: Data . . . . .	61
	LITERATURE CITED . . . . .	68

## LIST OF TABLES

Table		Page
I	Liquid Compositions for HCl-H <sub>2</sub> O at 19.95°C in Unsymmetric Convention . . . .	41
C-I	Binary Vapor-Liquid Equilibrium Data . . .	61
C-II	Physical Properties of Components . . . .	65

## LIST OF FIGURES

Figure		Page
1	Vapor Compositions of HCl-H <sub>2</sub> O System at 19.95°C using HVYFTW Program for Nonelectrolytes . . . . .	3
2	Dissociation Constant of HCl as a Function of Temperature . . . . .	11
3	Ionization of Hydrochloric Acid . . . . .	12
4	Experimental Equilibrium Mole Fractions for HCl-H <sub>2</sub> O System at 19.95°C . . . . .	14
5	Dependence of HCl Vapor Pressure on Concentration . . . . .	16
6	Vapor Compositions for NH <sub>3</sub> -H <sub>2</sub> O at Two Atmospheres . . . . .	30
7	Vapor Compositions for HF-H <sub>2</sub> O at One Atmosphere . . . . .	31
8	Vapor Compositions for HBr-H <sub>2</sub> O at 54.5°C . . . . .	33
9	Vapor Compositions for HCl-H <sub>2</sub> O at 19.95°C . . . . .	34
10	Vapor Compositions for HCl-H <sub>2</sub> O at 75°C . . . . .	37
11	Vapor Compositions for HCl-H <sub>2</sub> O at 55.2°C . . . . .	38
12	Vapor Compositions for HCl-H <sub>2</sub> O at 1.0 Atmosphere . . . . .	39

## ABSTRACT

An investigation has been made into vapor-liquid equilibrium for binary monovalent electrolyte systems. These electrolyte systems were treated as systems which deviate from nonelectrolyte behavior due to their dissociation in the liquid phase. Corrections to this nonelectrolyte behavior were made in fitting programs written to predict phase equilibrium for nonelectrolytes.

Improvements were made in the fitting programs for hydrochloric acid by considering the mole fraction of undissociated electrolyte molecules in the liquid phase as the liquid phase solute concentration. This undissociated molecule concentration was obtained from a concentration dependent dissociation curve.

Slightly dissociating electrolytes such as ammonia seem to differ much less from nonelectrolyte behavior than do highly dissociating electrolytes such as hydrochloric and hydrobromic acid.

## I. INTRODUCTION

When designing separation equipment involving distillation, it is necessary to have available data on vapor-liquid equilibrium for the components involved. There is some experimental data for binary systems, but much less is available for ternary and higher order systems due to the increased difficulty involved in the experimental work. Thus it would be desirable to have available a method of calculating multi-component vapor-liquid equilibrium requiring only component physical properties and equilibrium data from binary systems. First, however, a model would have to be devised to predict binary data using parameters obtained from binary data.

J. M. Prausnitz and co-workers at the University of California at Berkeley, have devised such a method to not only fit binary data but predict multicomponent data with good accuracy for nonelectrolytes at low or moderate pressures. They have published this work in the form of a series of programs in Computer Calculations for Multicomponent Vapor-Liquid Equilibria. Using component properties, binary equilibrium data, correlations for calculating some thermodynamic functions, and thermodynamic relations, the programs calculate certain parameters which are useful for predicting



multicomponent equilibrium values. While these programs give good fit to nonelectrolyte systems tested, they give poor results for almost all electrolyte systems. An example of the fit obtained can be seen in Figure 1, for a hydrochloric acid-water system. Thus in order to use these programs to calculate vapor-liquid equilibrium for electrolyte systems certain modifications must be made. While Prausnitz' monograph represents an attempt to summarize thermodynamic functions valid for nonelectrolytes into a computer program, this report represents an attempt to modify those programs to make them valid for acid and base electrolytes, particularly hydrochloric acid.

#### Nonelectrolyte Vapor-Liquid Equilibrium

The basic concepts used in the computer programs written by Prausnitz is that, 1) the sum of the mole fractions in both the liquid and the vapor phases is equal to 1.0, and, 2) the fugacity of each component in the liquid phase is equal to its fugacity in the vapor phase when the system is at equilibrium. The fugacities of the components are calculated using either experimental data or correlations which give good results. Since computers are used to do the calculations no assumptions of ideality need to be made. The calculation of the fugacities is reduced to using properties of the system or of the components involved.

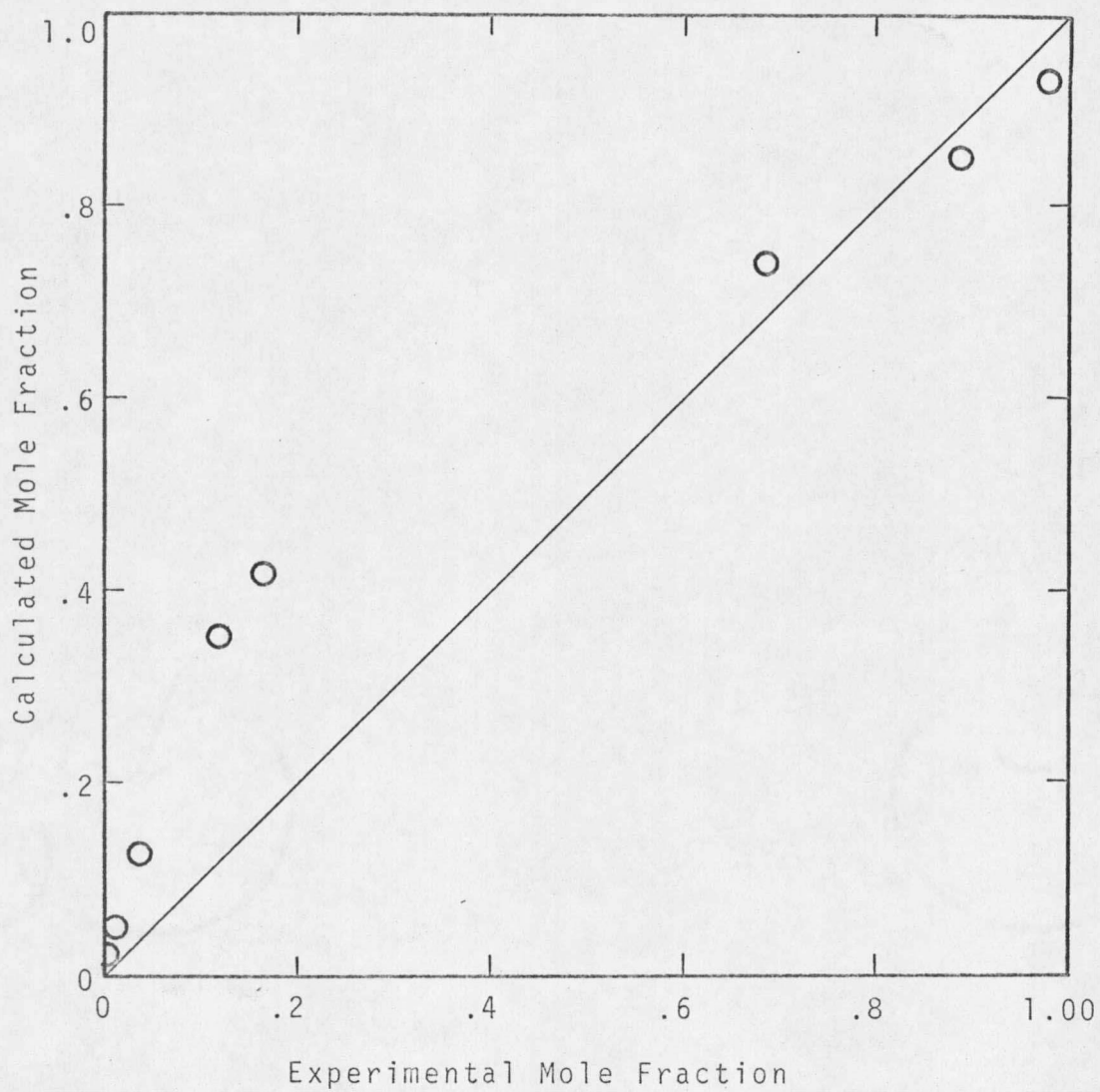


Figure 1. Vapor Compositions of HCl-H<sub>2</sub>O System at 19.95°C using HVYFTW Program for Nonelectrolytes.

The vapor phase fugacity of a component is related to its mole fraction by the following:

$$f_i^V = y_i \phi_i P$$

where

$f_i^V$  = vapor phase fugacity of component i.

$y_i$  = vapor phase mole fraction

$\phi_i$  = fugacity coefficient

$P$  = system pressure.

The fugacity is actually just the partial pressure corrected by the fugacity coefficient (in an ideal system,  $\phi_i \equiv 1.0$  and fugacity = partial pressure). A thermodynamic derivation by Beattie (16) gives a relation for the fugacity coefficient as a function of an equation of state of the vapor phase.

The liquid phase fugacity is a function of the liquid phase mole fraction according to the following relation:

$$f_i^L = x_i \gamma_i f_i^{oL}$$

where

$f_i^L$  = liquid phase fugacity of component i

$x_i$  = liquid phase mole fraction

$\gamma_i$  = activity coefficient

$f_i^{oL}$  = reference state fugacity.

There are thus two thermodynamic functions and one system variable upon which the liquid phase fugacity is dependent. Methods were needed to calculate the activity coefficient and reference state fugacity using only system properties.

The activity coefficient can be calculated using a thermodynamic relation involving the excess Gibbs free-energy of a system. The activity coefficients and mole fractions must also satisfy the Gibbs-Duhem expression,

$$\sum_{i=1}^N x_i d \ln \gamma_i = 0 \text{ (constant temperature and pressure)}$$

The excess Gibbs energy function used to calculate the activity coefficient is the following

$$RT \ln \gamma_i = \left( \frac{\partial n_T g^E}{\partial n_i} \right)_{T, P, n_j (j \neq i)}$$

where

$n_i$  = number of moles of  $i$

$n_T$  = total number of moles

$g^E$  = excess Gibbs energy

$R$  = gas constant

$T$  = temperature

$P$  = pressure.

Many models have been proposed as solutions to these two relations including the van Laar and Margules models.

Prausnitz chose to use a more recently developed model, the Wilson equation, which gave better accuracy than any of the previous ones.

The Wilson model is characterized by interaction parameters between solute and solvent. They are used as solutions

to the excess Gibbs energy which is defined as

$$\frac{g^E}{RT} = \sum_i x_i \ln \gamma_i = \sum_i \frac{n_i}{n_T} \ln \gamma_i$$

The Wilson equation is

$$\frac{g^E}{RT} = \sum_i x_i \ln \left[ \sum_{j=1}^N \Lambda_{ij} x_j \right]$$

where

$$\begin{aligned} \Lambda_{ij} &= \text{Wilson parameters} \\ &= \frac{v_j^L}{v_i^L} \exp \left[ - \frac{(\lambda_{ij} - \lambda_{ii})}{RT} \right] \end{aligned}$$

and

" $(\lambda_{ij} - \lambda_{ii})$  is an empirically determined energy term closely related to the difference in cohesive energy between an i-j pair and an i-i pair." (16)

By performing the indicated operation on the excess Gibbs energy, equations are obtained which give the activity coefficients of the binary system as solutions.

Prausnitz uses two methods by which the activity coefficient is standardized for the given component. For components which are at subcritical conditions in the system the activity coefficient approaches 1.0 as the mole fraction approaches 1.0, or

$$\lim_{x_i \rightarrow 1} \gamma_i = 1.0$$

$$x_i \rightarrow 1$$

If a component is supercritical, i.e. the system temperature is higher than the component's critical temperature, then the activity coefficient is defined to approach unity as the mole fraction approaches zero, or

$$\lim_{x_i \rightarrow 0} \gamma_i = 1.0$$

If a supercritical component exists, it is designated as the solute. When both components in a binary mixture are subcritical, they are treated the same and the symmetric convention is used. If one is subcritical and one is supercritical the components are in the unsymmetric convention. Activity coefficients for subcritical components are calculated by the above method from the excess Gibbs energy, while the activity coefficients for supercritical components are calculated from a method developed by Prigogine and Defay. This method is shown by O'Connell and Prausnitz (13) as

$$\frac{\gamma_i}{\gamma_{i*}} = \lim_{x_i \rightarrow 0} \gamma_i$$

where

$\gamma_i$  = activity coefficient in symmetric convention

$\gamma_{i*}$  = activity coefficient in unsymmetric convention.

The unsymmetric convention also assumes that the interaction parameter  $\Lambda_{21} = 0$ , where 1 represents the supercritical solute and 2 represents the subcritical solvent.

The second thermodynamic function characterizing the liquid phase fugacity is calculated differently for the two conventions. The reference state fugacity for a condensable component is that of the pure liquid at the system temperature and a reference pressure. It is calculated by equating the pure liquid fugacity to the fugacity of the pure saturated vapor at equilibrium.

Noncondensable components, for which the unsymmetrical convention is used, are usually present in low concentrations in the solutions. The reference state fugacity for these components is set equal to the Henry's constant for that component in the solvent. Thus the noncondensable components are assumed to follow fairly closely to Henry's Law, which is applicable to components at low concentrations.

#### Characteristics of Electrolyte Solutions

Electrolyte solutions are characterized by the presence of ions when the solvent used is a polar compound. These ions produce many of the effects present in electrolyte solutions such as conductance and nonideality. When the electrolyte is dissolved in the solvent the degree to which it dissociates is dependent on the bonds holding the molecule together and by the polarity of the solvent molecule. Electrolytes which form primarily ionic bonds dissolve and dissociate in a polar solvent much more easily than those

which exist as covalent molecules.

Electrolytes are classified into two primary groups. True electrolytes exhibit conductance characteristics out of solution and completely dissociate in solution. They may exist as ionic lattice crystals in their usual solid salt state, i.e., NaCl. Potential electrolytes, which include most acids and bases, do not dissociate out of solution and do not serve as conductors unless dissolved. Their dissociation is not complete, i.e., not 100% of all molecules dissociate, but some remain in solution as covalent molecules. It is these electrolytes with which we are concerned because they exert a vapor pressure and can thus be separated by distillation. Hereafter the term electrolyte will refer to these compounds.

Water is a particularly good solvent for electrolytes because of the polarity of the water molecule. The charge placement in the water molecule and in the electrolyte molecule cause an attraction between oppositely charged parts of the two molecules. If this attractive force is great enough, the electrolyte might dissociate into positive and negative ions in the case of an acid, or the water might dissociate in the case of a base. One of the ions may become attached to the other polar molecule in the solution and the other ion will exist by itself. When an acid is dissolved in water it dissociates as follows:









































































































































