



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
Montana State University
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Abstract:

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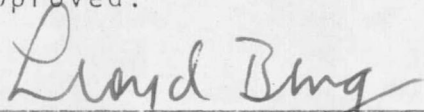
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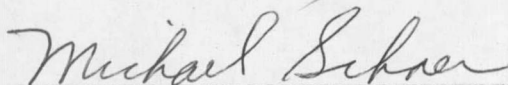
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ABSTRACT

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.

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.

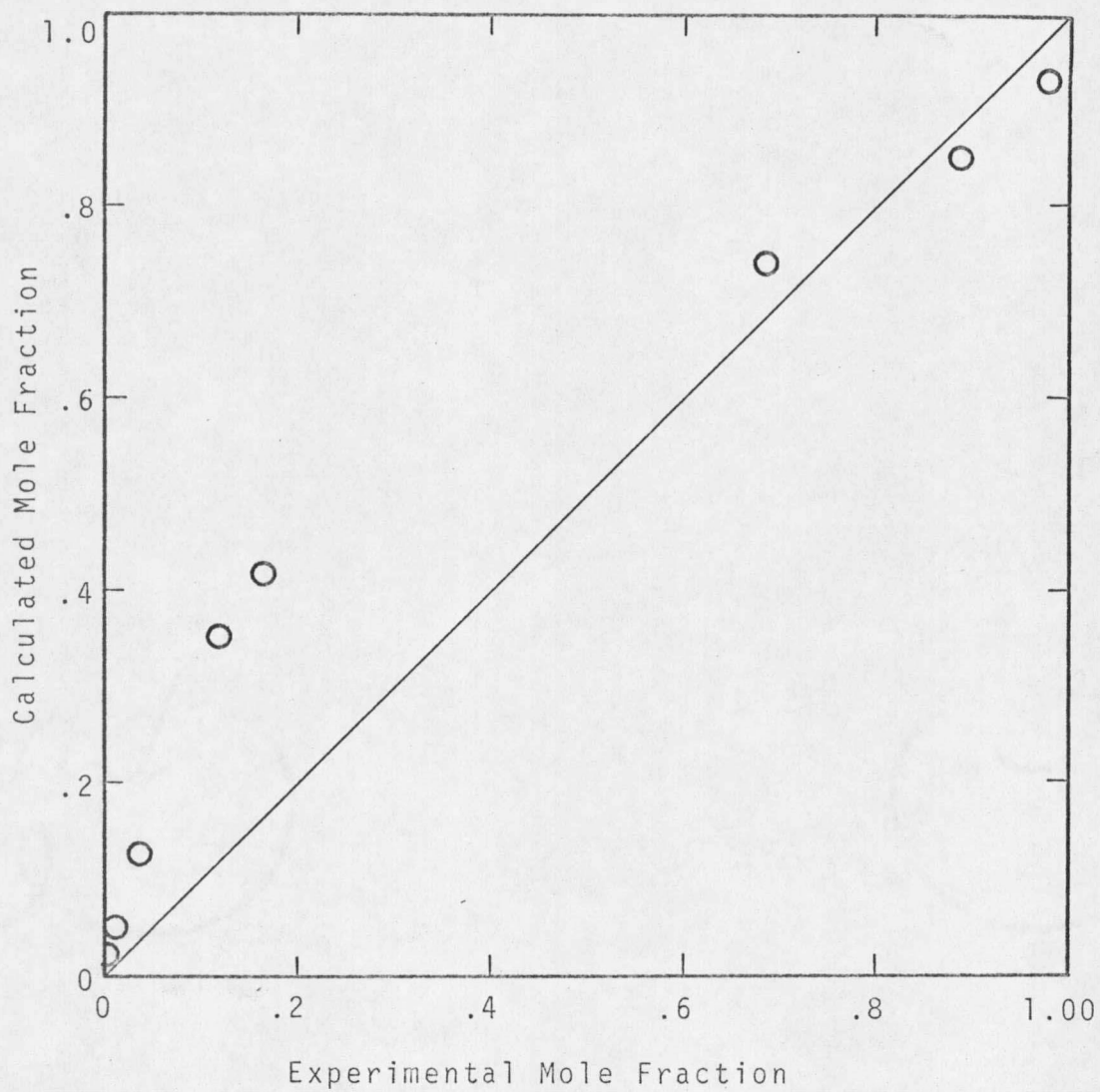


Figure 1. Vapor Compositions of HCl-H₂O System at 19.95°C using HVYFTW Program for Nonelectrolytes.

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

ϕ_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

γ_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

γ_i = activity coefficient in symmetric convention

γ_{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.

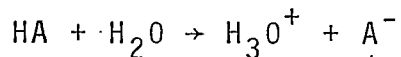
Characteristics of Electrolyte Solutions

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:



The amount of ionization or dissociation occurring is governed by a dissociation constant for the reaction. This constant is defined for the acid dissociation as:

$$K_{\text{diss}} = \frac{a_{\text{H}_3\text{O}^+} a_{\text{A}^-}}{a_{\text{HA}} a_{\text{H}_2\text{O}}}$$

where a = activity of the chemical entity.

The activity is related to the mole fraction by the activity coefficient in the particular solution

$$a_{\text{B}} = \gamma_{\text{B}} \cdot x_{\text{B}}$$

The dissociation of a compound is dependent on both temperature and concentration as shown in Figures 2 and 3 for HCl in water.

Since electrolytes exist in the vapor phase not as ions but as covalent molecules, they must also be present as covalent molecules in the liquid phase. The covalent molecule mole fraction in the liquid phase may be determined by the dissociation constant of the particular electrolyte. This constant is not the same for all electrolytes but is dependent on the electrolyte bond strength. Hydrochloric acid is a particularly highly dissociating acid with a dissociation constant of about 10^7 . Ammonia and hydrofluoric acid are much weaker and have a dissociation constant in the region of 10^{-4} to 10^{-5} .

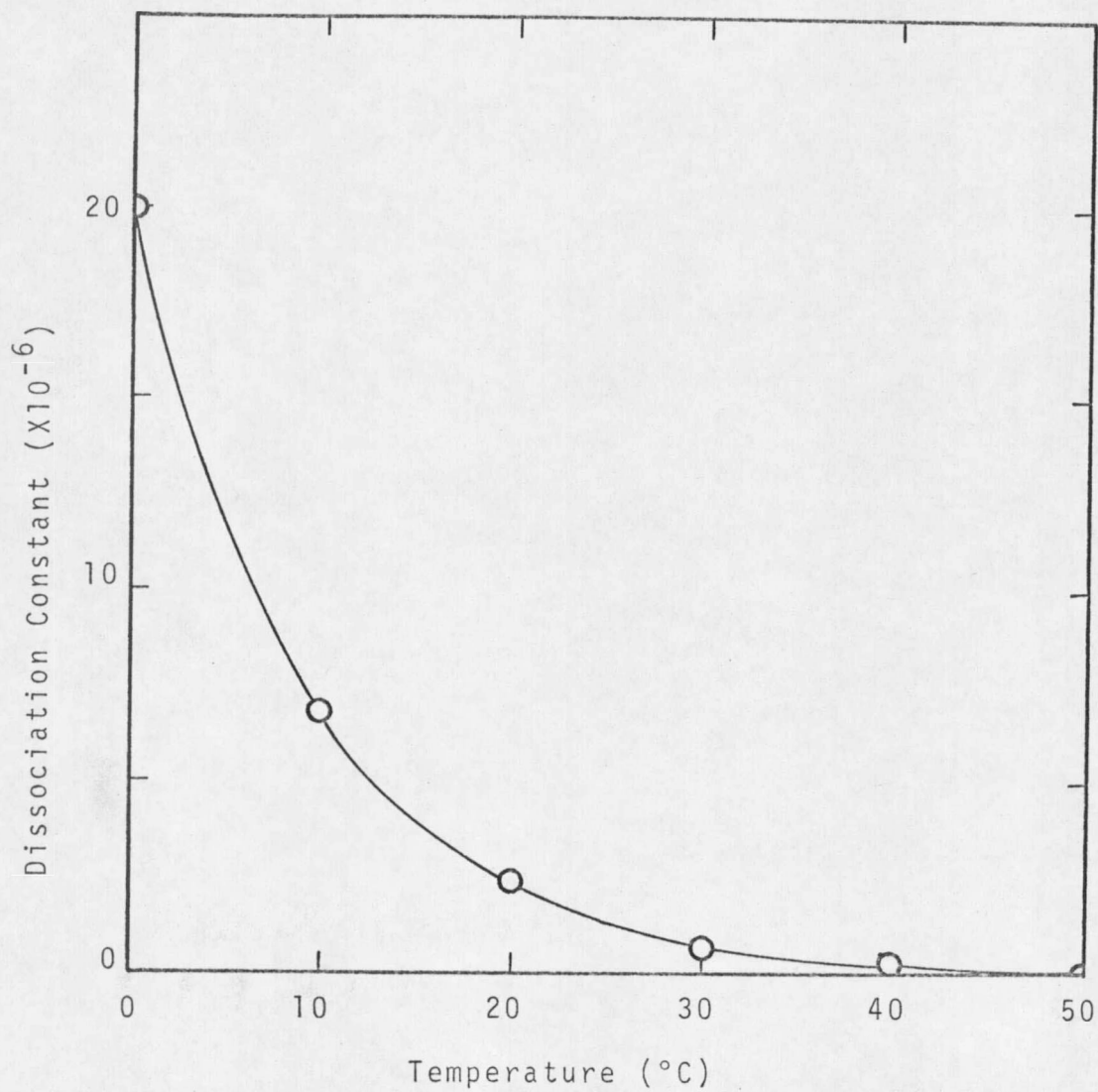


Figure 2. Dissociation Constant of HCl as a Function of Temperature.

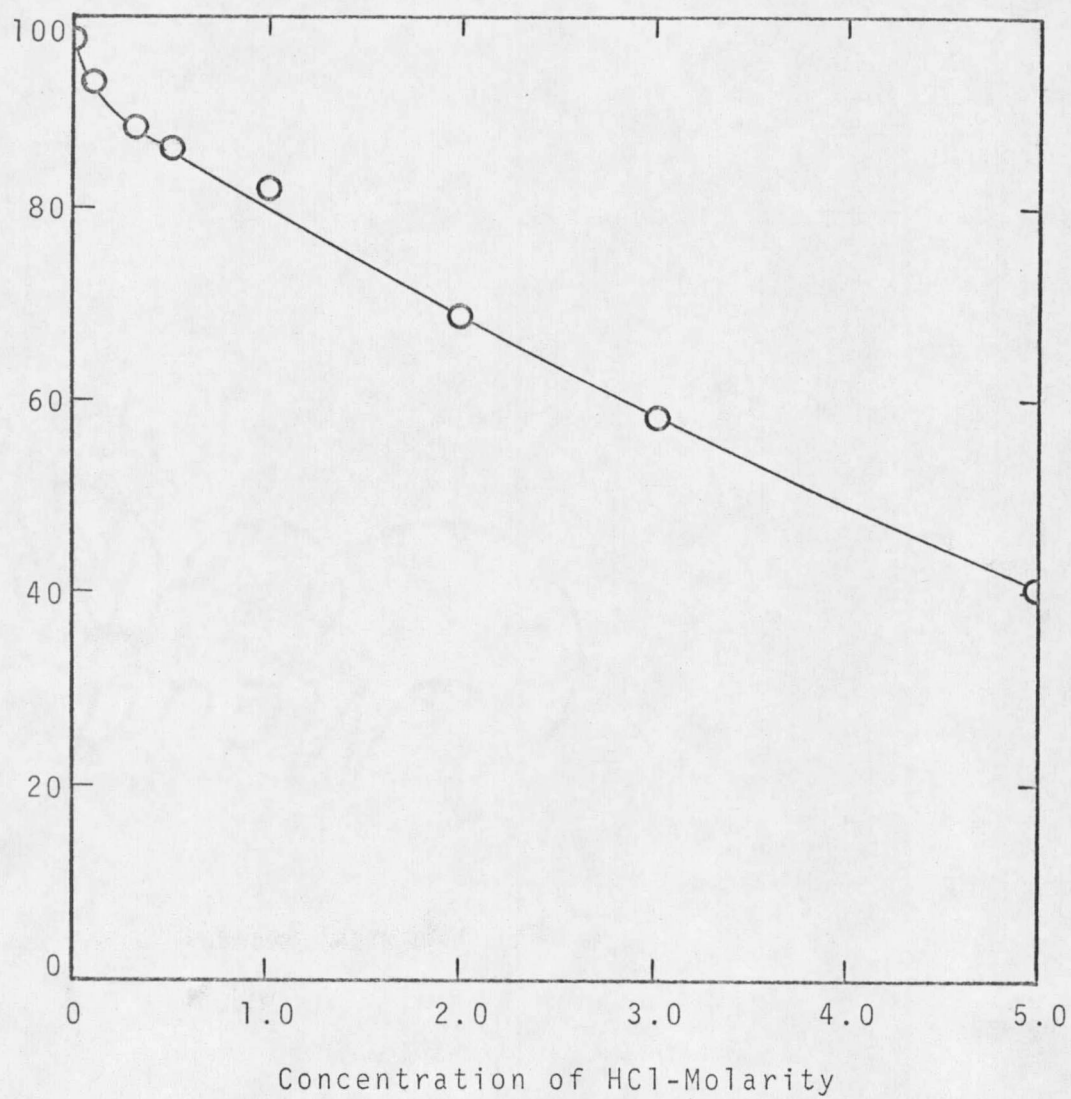


Figure 3. Ionization of Hydrochloric Acid

The deviation from ideality of one particular electrolyte, hydrochloric acid, in water, may be observed by looking at Figure 4. No solution is truly ideal, but the hydrochloric acid solution is much farther from ideality than any nonelectrolyte system observed except those containing a noncondensable or supercritical component. Since the acid solution is at 19.95°C, and below its critical point, its nonideality apparently does not exist as a result of its being a supercritical component. Robinson and Stokes (19) discussed the nonideality of hydrochloric acid: "At 10 N, ..., the partial pressure of hydrogen-chloride is of the order of 20 mm, in contrast with a value of about 7.6 atm. which would be estimated from vapor pressure of pure liquid hydrogen chloride at 20° (41 atm) on the basis of Raoult's law if the hydrochloric acid were completely undissociated and an ideal solute. ..., This figure, ..., indicates that an appreciable amount (of the order of 0.3 percent) ... is in the form of covalent molecules."

Dissociation of electrolyte solutions results in two other effects. One effect is caused by the presence of charged particles in solution. These charged particles produce long-range electrostatic interactions between the ions in addition to van der Waals and other shorter range forces commonly present in solutions.

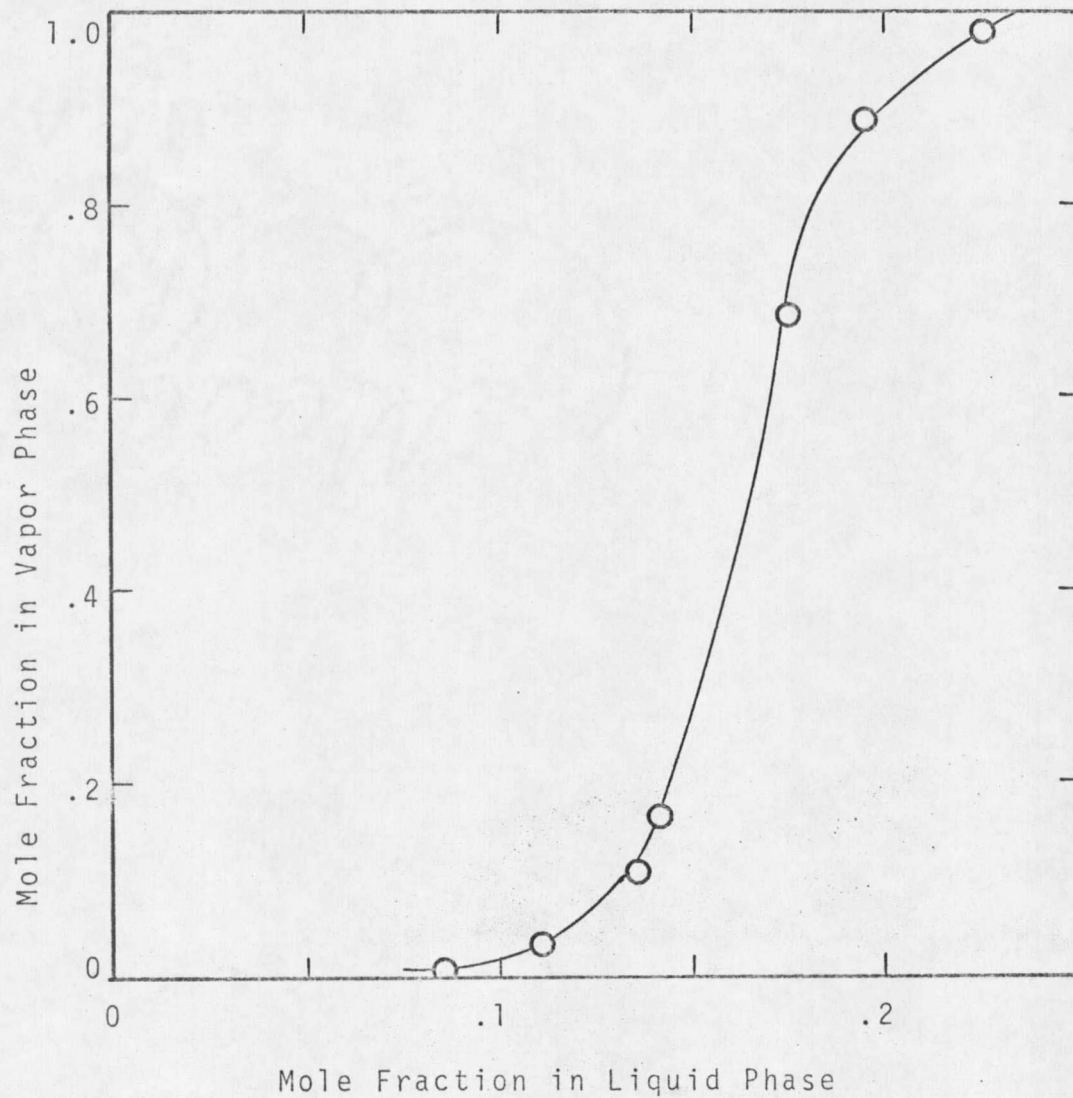


Figure 4. Experimental Equilibrium Mole Fractions for HCl-H₂O System at 19.95°C. (2)

The second effect of dissociation is the increase in the number of solute particles present in solution. Every time a molecule dissociates, another particle is formed. Thus the solute concentration would double in a completely dissociated electrolyte solution. The result of this increase is shown by Denbigh (6) where the vapor pressure of hydrochloric acid, a highly dissociating electrolyte, is shown as a function of concentration of solute. In Figure 5 the first curve shows vapor pressure as a function of the concentration of HCl in solution while the second curve shows vapor pressure as a function of concentration squared. The second curve approaches zero concentration at a finite slope as it should if it were to obey Henry's Law at low concentrations. The first curve has a slope of zero as it approaches zero HCl concentration. This dependence on the concentration squared may be a result of the existence of two moles of solute in solution for every mole dissolved.

Since many electrolytes dissociate into more than two ions (H_2SO_4 , H_3PO_4) there may be many different ions present in these solutions. Ions may associate in solution to form complexes other than the parent molecule in these solutions. Thus ions of valences of two or three may exist in some solutions in addition to the more common single valenced ion. Since this work is an initial probe into the field of electrolyte vapor-liquid equilibrium, only single valenced ions

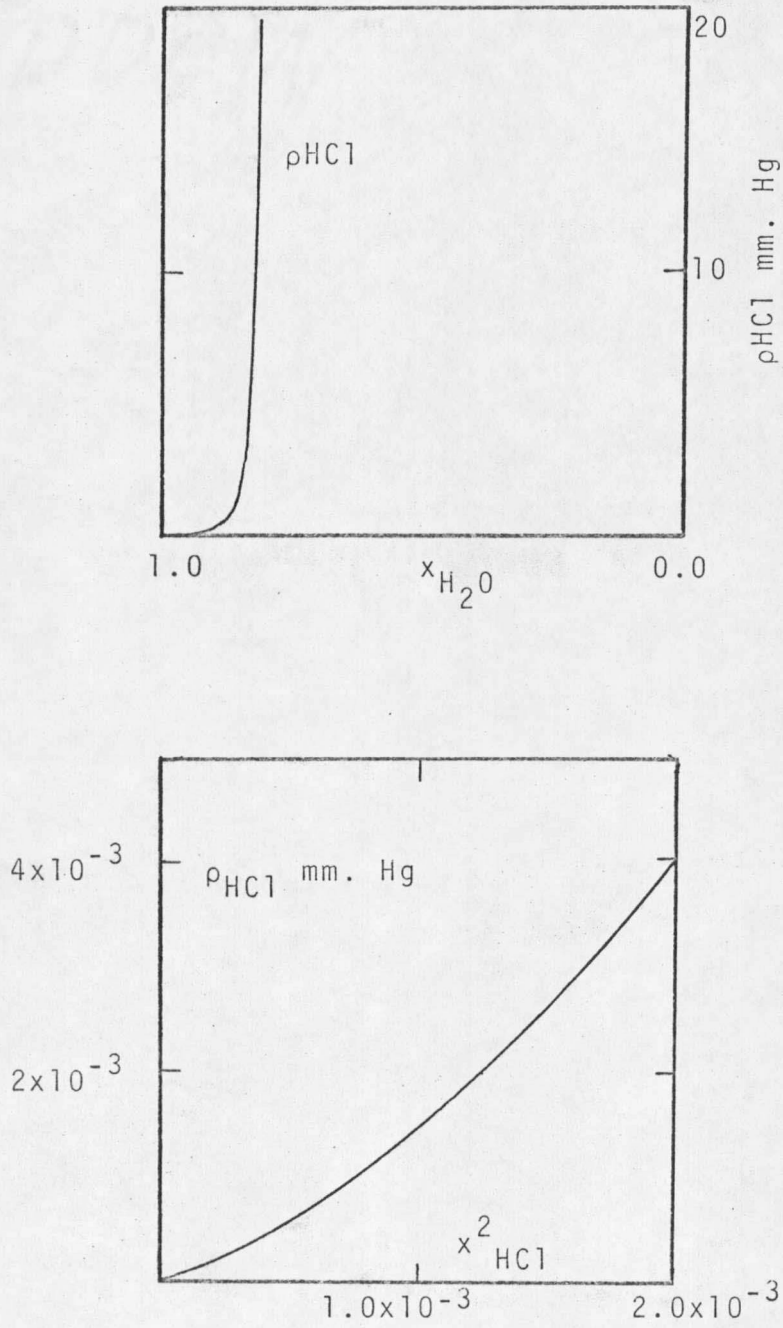


Figure 5. Dependence of HCl Vapor Pressure on Concentration (6).

will be considered. This will reduce the complexity of the system. Hydrochloric acid is of primary interest because it is monovalent, highly nonideal, and more data are available on it than most other electrolytes.

Most work done on electrolyte solutions up to this time has been involved with conductivity and diffusion of electrolytes and basic functions related to or derived from these phenomena. Little work has been done on phase equilibrium and the thermodynamic quantities needed for its study. Hala (8) has devised a method for calculating vapor-liquid equilibrium for electrolytes using the excess Gibbs energy function derived from the free energy of dilution and employing a separation function for dissociation. However he does not equate fugacities in the vapor and liquid phases as a means of predicting equilibrium. According to Hala the excess Gibbs energy for an electrolyte is:

$$\Delta G_{\pm}^E = \sum_{i=1}^k n_i v_i RT \ln \gamma_{i\pm}$$

as compared to that for nonelectrolytes

$$\Delta G^E = n_T g^E = \sum_{i=1}^k n_i RT \ln \gamma_i$$

where

$$v_i = v_{i+} + v_{i-} = \text{total number of ions produced by dissociation}$$

$$\begin{aligned}\gamma_{i\pm} &= \text{ionic activity coefficient} \\ &= (\gamma_{i+}^{\nu_{i+}} \gamma_{i-}^{\nu_{i-}})^{1/\nu_i}\end{aligned}$$

From this function the ionic activity coefficient can be obtained

$$\left(\frac{\partial \Delta G_{\pm}^E}{\partial n_i}\right)_{T,P,n_j(i \neq j)} = \nu_i RT \ln \gamma_{i\pm}$$

If a model were used which was a solution to the excess Gibbs energy and satisfied the Gibbs-Duhem equation, it could be used to calculate the ionic activity coefficient by means of the last relation.

The standard state for electrolytes is defined such that the activity coefficient of the electrolyte approaches unity as the concentration of the electrolyte approaches zero. This is similar to the unsymmetric convention used for nonelectrolyte systems containing noncondensables.

The activity coefficient of an electrolyte may be determined by conductivity experiments or theoretically from the Debye-Huckel method. However, the above procedure involving the excess Gibbs energy is more interesting in this work since it involves a method which could be programmed and one which will yield physical parameters describing a system. If a model were developed which would

satisfy the Gibbs-Duhem equation and accurately predict ionic activity coefficients, it would be valuable in phase equilibria for electrolytes.

II. STATEMENT OF THE PROBLEM

Although there has been work done to obtain vapor-liquid equilibrium data for nonelectrolyte systems with good accuracy, this method yields poor results when applied to electrolyte systems. Prausnitz' work has been summarized in the form of computer programs to obtain the equilibrium data for multi-component systems using only binary equilibrium data. Fitting programs are used to obtain parameters for the binary systems which describe these systems and can then be used for the multicomponent systems.

Hala (8) has derived a method for obtaining vapor-liquid equilibrium for electrolyte systems with good results for the systems tested but his method is much different than that used by Prausnitz. It does not use many basic phase equilibrium thermodynamics functions and relations and does not equate fugacities in the liquid and vapor phases.

Since no real attempt has been made to summarize thermodynamic functions for electrolytes as has been done for nonelectrolytes, this report represents an initial attempt to do this. The fitting programs of Prausnitz will be modified to predict vapor-liquid equilibrium for binary systems of extremely non-ideal electrolytes such as hydrochloric acid. If this objective were accomplished then attempts could be made to use these fitting programs to obtain parameters which

would be used for multi-component systems.

Thus the objectives of this investigation were the following:

1. Make corrections on the theory of nonelectrolytes to include effects produced by electrolyte dissociation characteristic of electrolyte solutions.
2. Use these corrections to revise Prausnitz' fitting programs to predict vapor-liquid equilibrium for binary electrolyte solutions, particularly hydrochloric acid.

III. PROCEDURE

There were two basic methods used in this research in an effort to obtain a correction of Prausnitz's programs which would predict vapor-liquid equilibrium for electrolytes. The first method was to calculate the mole fraction of covalent molecules present in a system at a given concentration of electrolyte and use this as the solute in the equilibrium liquid phase. The second method was to correct the excess Gibbs energy used by Prausnitz to calculate liquid phase activity coefficients to that excess Gibbs energy proposed by Hala for electrolytes.

Two different fitting programs were employed in the research. The first program was HVYFTW and its associated subroutine CALPHW used by Prausnitz for systems treated in the symmetric convention. The second fitting program was LTFTXW and its associated subroutine CALXLW for components treated in the unsymmetric convention. These subroutines are used to calculate activity coefficients for the particular convention employed. Both programs also use the subroutines INPUT, for converting input data to suitable form; VIRIAL, for calculating the second virial coefficient of the gas mixture; RSTATE, for calculating reference state fugacities and partial molar volumes; PHIMIX for calculating the fugacity coefficients of the components, and LSQ which is

used to obtain a least squares fit of the data.

Seven different sets of data taken from equilibrium data compiled by Chu (2), were used in testing the methods proposed for this research. These included water as the solvent with the electrolytes ammonia, hydrofluoric, hydrobromic, and four sets of hydrochloric acid. These data could all be used in the HVYFTW program, but only isothermal data can be used in LTFTVW. Because of its extreme nonideality, hydrochloric acid was the primary electrolyte studied. Hydrobromic acid is also a highly dissociating, nonideal electrolyte, but ammonia and hydrofluoric acid dissociate to a much smaller degree. Data on hydrochloric acid is much more common than that for hydrobromic acid so hydrochloric acid was studied more extensively.

The data included ammonia at two atmospheres, hydrofluoric acid at one atmosphere, hydrobromic acid at 54.5°C, and hydrochloric acid at 19.95°C, one atm., 55.2°C, and 75°C. These data are included in Appendix C along with other physical properties of the components.

In making corrections to Prausnitz programs, it was assumed that the vapor phase molecules are far enough apart that the molecules have little influence on each other. Since they also exist as covalent molecules in vapor, the vapor phase of electrolytes should be similar in behavior to that

of nonelectrolytes. Thus no changes were made in calculating vapor phase fugacities and only effects caused by dissociation in the liquid phase were included in the research.

Undissociated Liquid Phase Molecules

Since only covalent molecules exist in the vapor, they must be in equilibrium with covalent molecules in the liquid phase. The curve of dissociation of HCl molecules as a function of concentration (Figure 3) shows that dissociation decreases with increased concentration. It was thought that the great increase of vapor phase mole fraction with increasing liquid mole fraction in Figure 4, might be a result of this increase in covalent molecules in the liquid phase. By equating the fugacity of undissociated molecules in the liquid phase with the vapor phase fugacity, the vapor phase mole fraction should be calculated. The ions present in the solution would be considered as part of the solvent and not the solute.

This mole fraction of undissociated liquid phase electrolyte molecules was calculated by two methods. In the general case the mole fraction was calculated by subroutine COVCAL using dissociation constants for the particular electrolyte. The subroutines CUBIC and QUAD from McCormick (12) were used to solve a cubic equation in the calculation. This method of calculation is outlined in Appendix A, and the

subroutines are listed in Appendix B. The second method was used only for hydrochloric acid solutions using the dissociation curve in Figure 3. This curve was approximated by two straight lines initially and then fitted using a cubic equation. The method is outlined in Appendix B.

Excess Gibbs Energy

The second method used in correcting for electrolyte nonidealities consisted of calculating the ionic activity coefficient by using the Wilson equation as a solution to the excess Gibbs energy of dilution as proposed by Hala. This excess Gibbs energy is defined as:

$$-\Delta G_{\pm}^E = \sum_i^N n_i v_i RT \ln \gamma_{i\pm}$$

and is based on the complete dissociation of the electrolyte.

When the Wilson parameters are introduced as a solution to this, the excess Gibbs energy becomes

$$-\Delta G_{\pm}^E = -\sum_i^N n_i v_i RT \ln \left[\sum_{j=1}^k \Lambda_{ij} x_{j\pm} \right]$$

After differentiating the first expression with respect to moles of component i , an expression for the activity coefficient of i can be obtained.

$$\left(\frac{\partial (-\Delta G_{\pm}^E)}{\partial n_i} \right)_{T,P,n_j(j \neq i)} = v_i RT \ln \gamma_{i\pm}$$

Then by performing a similar operation on the second expression, an expression for the activity coefficient in terms of the Wilson parameters is obtained.

$$v_i = v_{i-} + v_{i+} = \text{total number of ions produced by complete dissociation}$$

$$\Lambda_{ij} = \text{Wilson parameter}$$

$$x_{i\pm} = \text{mole fraction of component after complete dissociation of solute}$$

$$= (x_{i+}^{v_{i+}} x_{i-}^{v_{i-}})^{1/v_i}$$

for monovalent electrolyte

$$x_{j+} = \frac{n_{j+}}{n_{j+} + n_{j-} + n_k}$$

$$n_{j+} = \text{moles of positive ion produced per mole of electrolyte}$$

$$n_{j-} = \text{moles of negative ion produced per mole of electrolyte}$$

$$n_k = \text{moles of solvent present per mole of electrolyte.}$$

The resulting expressions for activity coefficients of the electrolyte and the solvent are:

$$\gamma_{1\pm} = \exp\left[-x_{2\pm} \frac{x_{1\pm}^{-2} \Lambda_{12}}{x_{1\pm} + \Lambda_{12} x_{2\pm}} - x_{2\pm} \frac{x_{2\pm} \Lambda_{21}^{-2} x_{2\pm}}{\Lambda_{21} x_{1\pm} + x_{2\pm}}\right] / (x_{1\pm} + \Lambda_{12} x_{2\pm})$$

$$\gamma_{2\pm} = \exp\left[-v_1 x_{1\pm} \frac{2\Lambda_{12} x_{1\pm} - x_{1\pm}}{x_{1\pm} + \Lambda_{12} x_{2\pm}} - x_{2\pm} \frac{2x_{1\pm} - \Lambda_{21} x_{1\pm}}{\Lambda_{21} x_{1\pm} + x_{2\pm}}\right]$$

$$/ (\Lambda_{21} x_{1\pm} + x_{2\pm}),$$

where (1) refers to electrolyte
(2) refers to solvent in binary.

This operation as shown gives activity coefficients in the symmetric convention. The calculation procedure is shown in Appendix A.

The activity coefficients for the unsymmetric convention are calculated from symmetric convention activity coefficients using the following expression as shown by O'Connell and Prausnitz (13).

$$\frac{\gamma_{1\pm}^*}{\gamma_{1\pm}} = \lim_{x_{1\pm} \rightarrow 0} \gamma_{1\pm}$$

where $\gamma_{1\pm}^*$ = activity coefficient in unsymmetric convention.

The interaction parameter Λ_{21} was set equal to zero as done by Prausnitz assuming little solvent-solute interaction. The resulting activity coefficients for the unsymmetric convention are:

$$\gamma_{1\pm}^* = \exp\left(-x_{2\pm} \frac{x_{1\pm} - 2x_{1\pm}\Lambda_{12}}{x_{1\pm} + \Lambda_{12}x_{2\pm}} + \frac{2x_{2\pm}}{v_1} - \frac{2}{v_1} \frac{\Lambda_{12}}{x_{1\pm} + \Lambda_{12}x_{2\pm}}\right)$$
$$\gamma_{2\pm} = \exp\left(-v_1 x_{1\pm} \frac{2\Lambda_{12}x_{1\pm} - x_{1\pm}}{x_{1\pm} + \Lambda_{12}x_{2\pm}} - 2x_{1\pm}\right) / x_{2\pm}$$

This calculation is shown in Appendix A and is listed in Appendix B as it appeared in the program.

Since the activity coefficient of electrolytes is normalized to approach unity as the mole fraction approaches zero, they should be treated in the unsymmetric convention. The reference state fugacity should be Henry's constant, and the program LTFTXW should apply because it contains both these features. Both conventions were tested in an effort to obtain mole fractions which fit the data.

IV. RESULTS

The original fitting programs were initially run with five sets of binary data: NH_3 , HF, HBr, and two sets of HCl data. The $\text{NH}_3\text{-H}_2\text{O}$ system attained good fitting results using the symmetric convention fitting program. These results are shown in Figure 6. This data set was not used in the unsymmetric convention because only isothermal data can be used in that fitting program. The close fit obtained for the ammonia system may be due to the small amount of dissociation that ammonia undergoes in solution. This would make the ammonia more nearly like the undissociated nonelectrolytes than the more highly dissociating hydrochloric acid. These results were good enough that no real correction is probably needed for ammonia.

Hydrofluoric acid dissociates only slightly more than ammonia as evidenced by a comparison of their dissociation constants, 6.75×10^{-4} for HF and 1.78×10^{-5} for NH_3 . However, the fit obtained for HF as shown in Figure 7, was much poorer than for NH_3 in the symmetric convention and no improvement was made upon introducing the corrections for dissociation. The mole fractions obtained from the corrected excess Gibbs energy were worse than the uncorrected calculations and the change made by using only the covalent molecules present in calculating the mole fraction made little

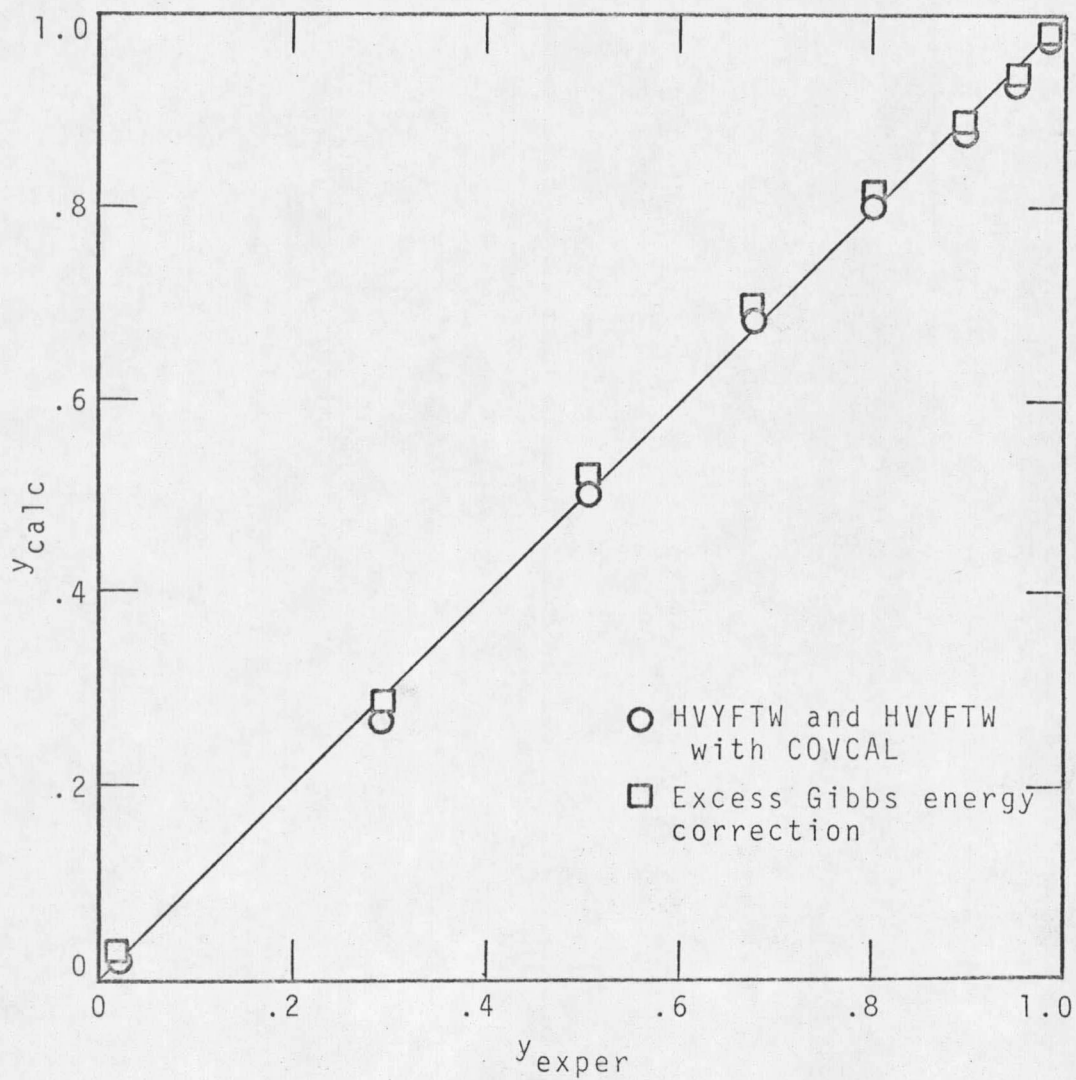


Figure 6. Vapor Compositions for $\text{NH}_3\text{-H}_2\text{O}$ at 2 atmospheres.

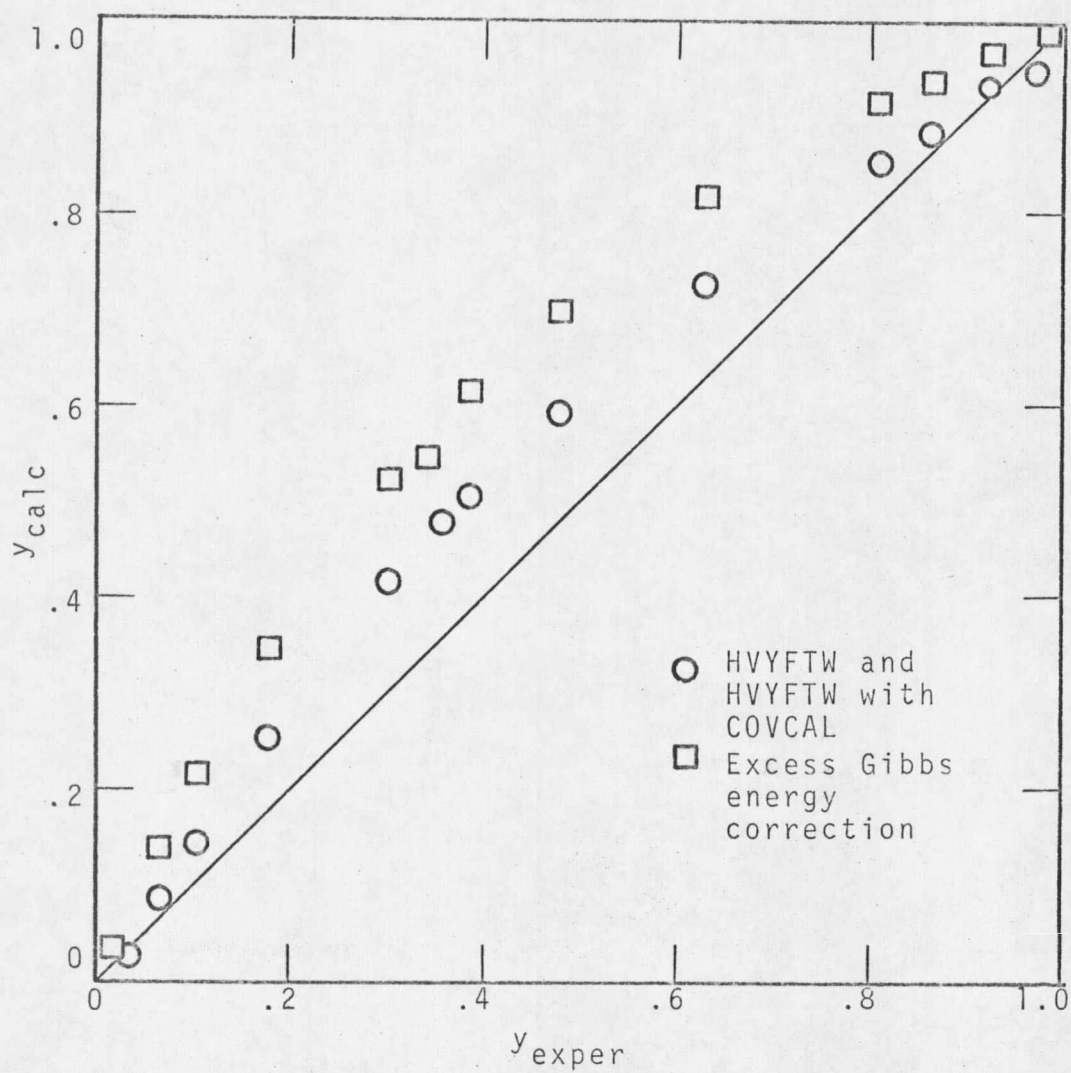


Figure 7. Vapor Compositions for HF-H₂O
at 1.0 Atm.

difference. The unsymmetric convention wasn't used because this data was for isobaric and not isothermal conditions.

Hydrobromic acid dissociates much more than hydrofluoric acid and the uncorrected symmetric convention fitting program, HVYFTW, yields vapor phase mole fraction values which are far above experimental. This would be expected if there are less covalent molecules present in the liquid than indicated by the original mole fraction. The original HVYFTW program calculates properties based on mole fraction of solute. However, the use of subroutine COVCAL apparently overcorrects for this. The dissociation constant of HBr was unavailable so that for HCl, 10^7 was used. This gave vapor phase concentrations of zero so the mole fraction of covalent molecules in the liquid phase must have been too low. The corrected excess Gibbs energy gave better results but they were still much too high. These results are shown in Figure 8.

The HCl data tested most was that at 19.95°C. The results of the four methods involving the HVYFTW program are shown in Figure 9. It is easily seen that the results obtained from the theory using the undissociated electrolyte as liquid phase mole fraction calculated from the dissociation curve are the best. These results are still in error but show a great improvement over the other methods used. The

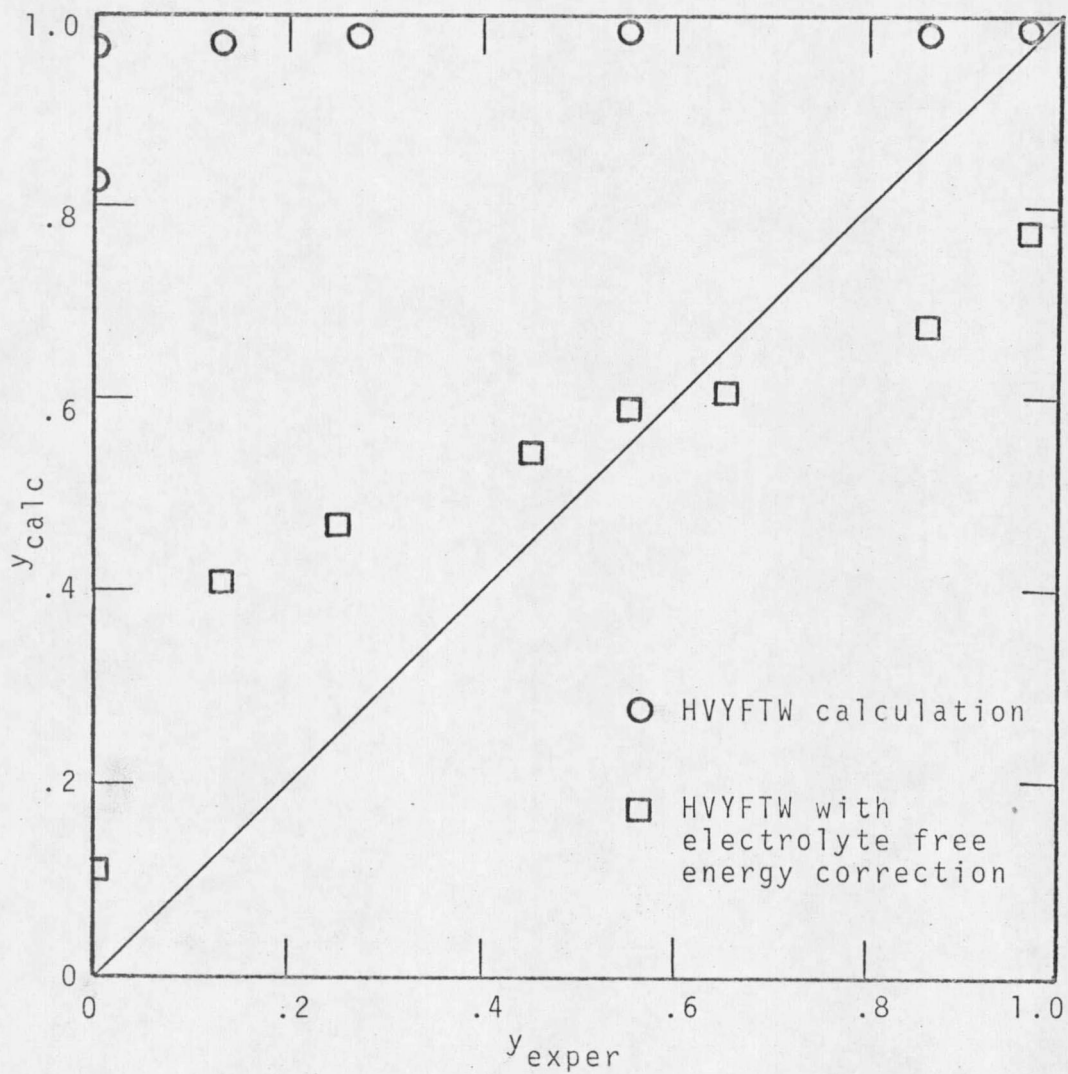


Figure 8. Vapor Compositions for HBr-H₂O at 54.5°C.

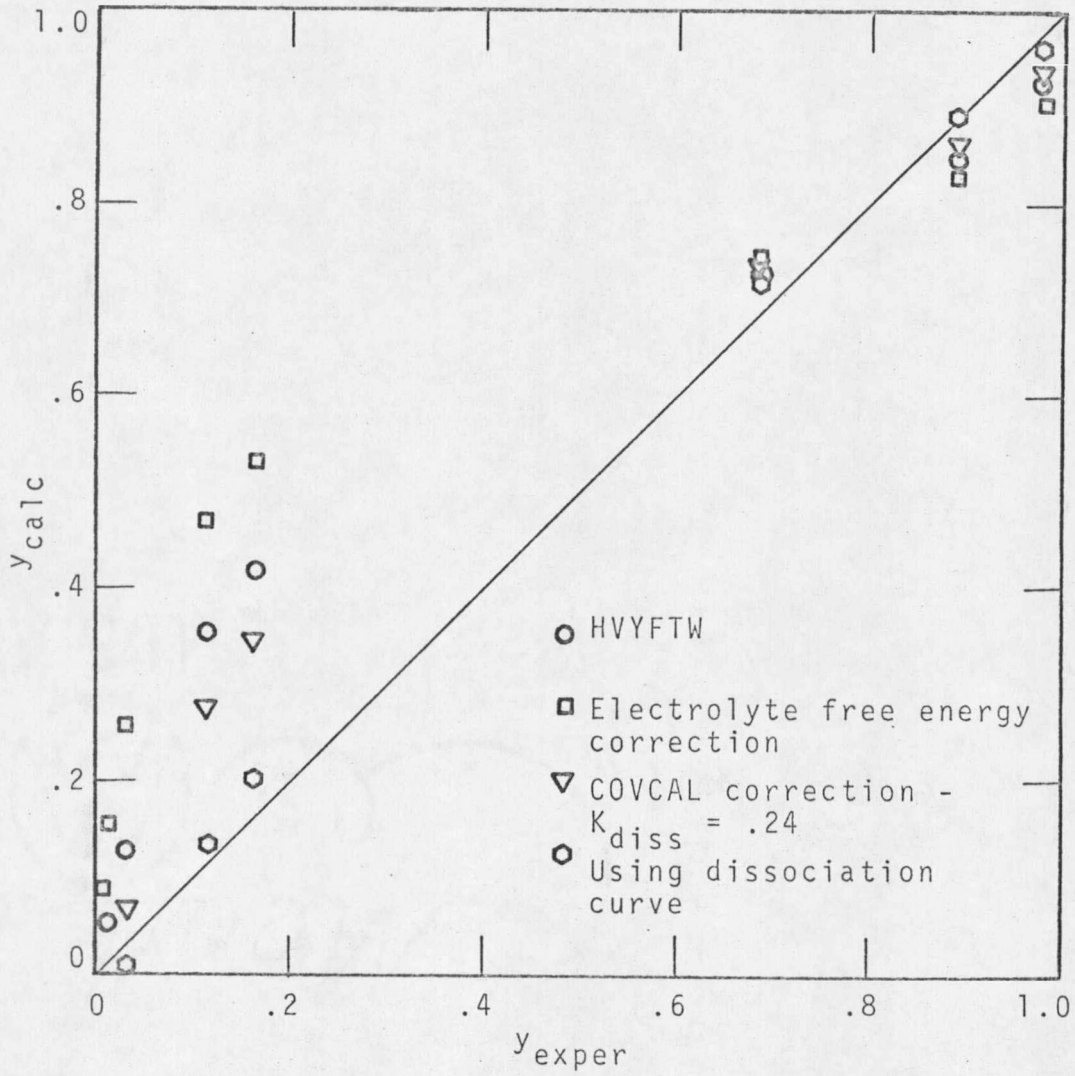


Figure 9. Vapor compositions for HCl-H₂O at 19.95°C.

conditions under which this curve was obtained are not given by Curtman (4), but it was probably at 25°C. The results obtained from the excess Gibbs energy for electrolytes proposed by Hala and based on complete dissociation of the electrolyte yields the poorest results. This seems strange since this method gave good results for ammonia, which does not dissociate greatly, and represented an improvement for HBr which does dissociate greatly.

The calculation of the covalent molecules by the subroutine COVCAL, which uses a dissociation constant, yielded the second best results. However a dissociation constant of .24 was used rather than 2.5×10^7 as obtained by Wynne-Jones (21). The latter was tried but yielded mole fractions of the near zero in the vapor phase. This might indicate that, 1) the dissociation constant of 2.5×10^7 should not be used although Robinson (18) obtained a similar one, or, 2) the assumptions used in calculating the covalent mole fraction were poor (activity coefficients = 1.00). However these latter assumptions should not make a great deal of difference. The mole fractions of liquid phase covalent molecules were calculated in a separate program and gave values much less than those obtained from the dissociation curve. Thus the dissociation constant may be a poor way of calculating mole fractions. It did not have a dependence on concentration either.

The HCl data at 75°C was fit best by the dissociation curve as shown in Figure 10. The original HVYFTW program predicted values much too high. The correction using the Gibbs function for electrolytes predicted values too high except at higher concentrations while the dissociation curve predicted values which were low but fairly consistent. This data was not tested using the COVCAL subroutine to calculate the covalent molecule mole fraction with the dissociation constant of .24.

The method of determining phase equilibrium properties from the presence of covalent solute molecules in the liquid-phase using the dissociation curve for HCl was then tested with two more HCl systems. The first, at 55.2°C, gave fairly good results as shown in Figure 11, but the second, at one atmosphere, gave results which were very low in Figure 12. However, an error developed during the program calculation for the second data set and the results may not have been valid. These poor results may also have been due to the changing of the temperature of the system over the mole fraction range. The dissociation is not constant over a temperature range but varies as does the dissociation constant. Some of the data may have been out of the range of the temperature at which the curve was obtained. However this is only speculation.

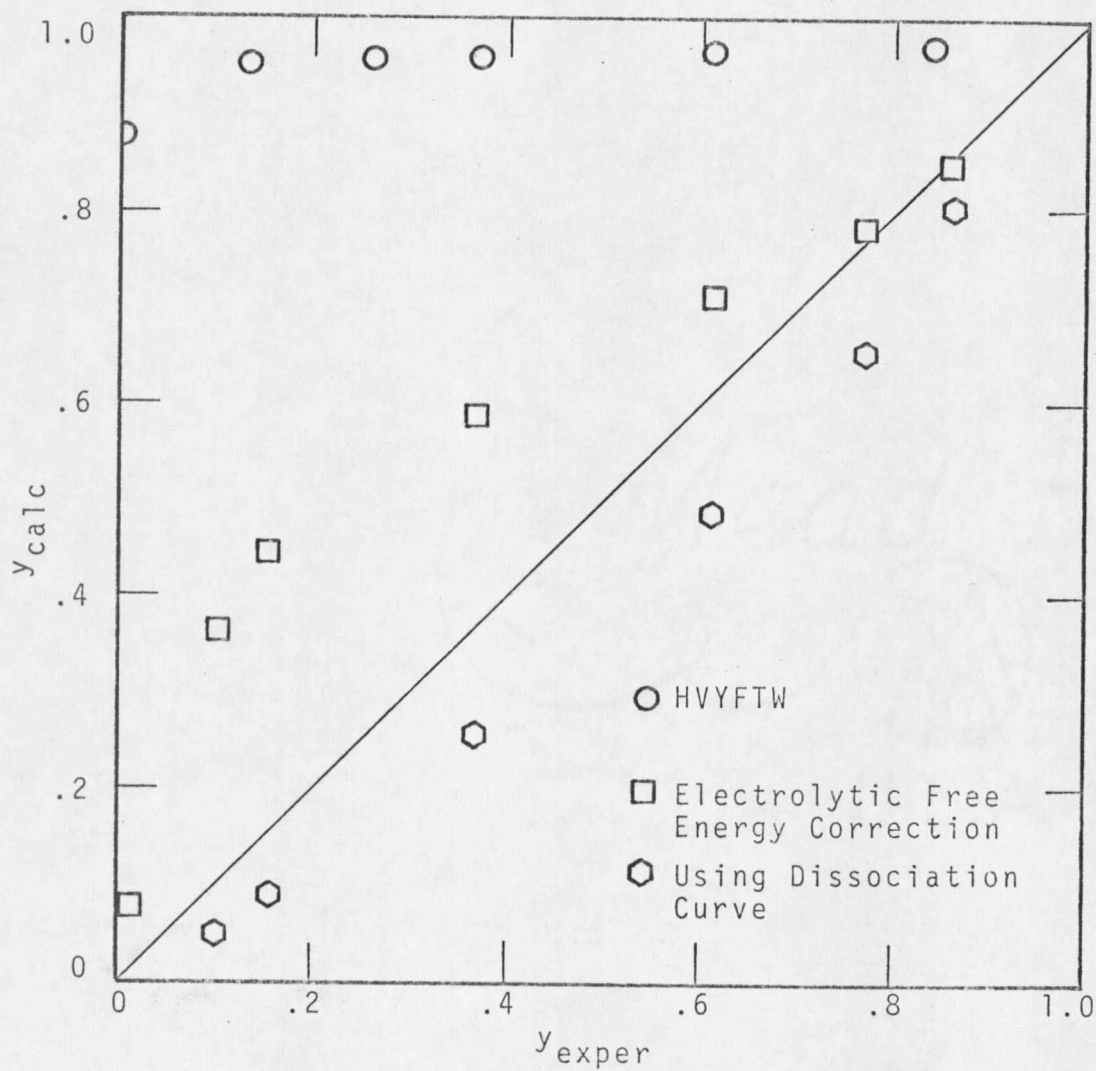


Figure 10. Vapor Compositions for HCl-H₂O at 75°C.

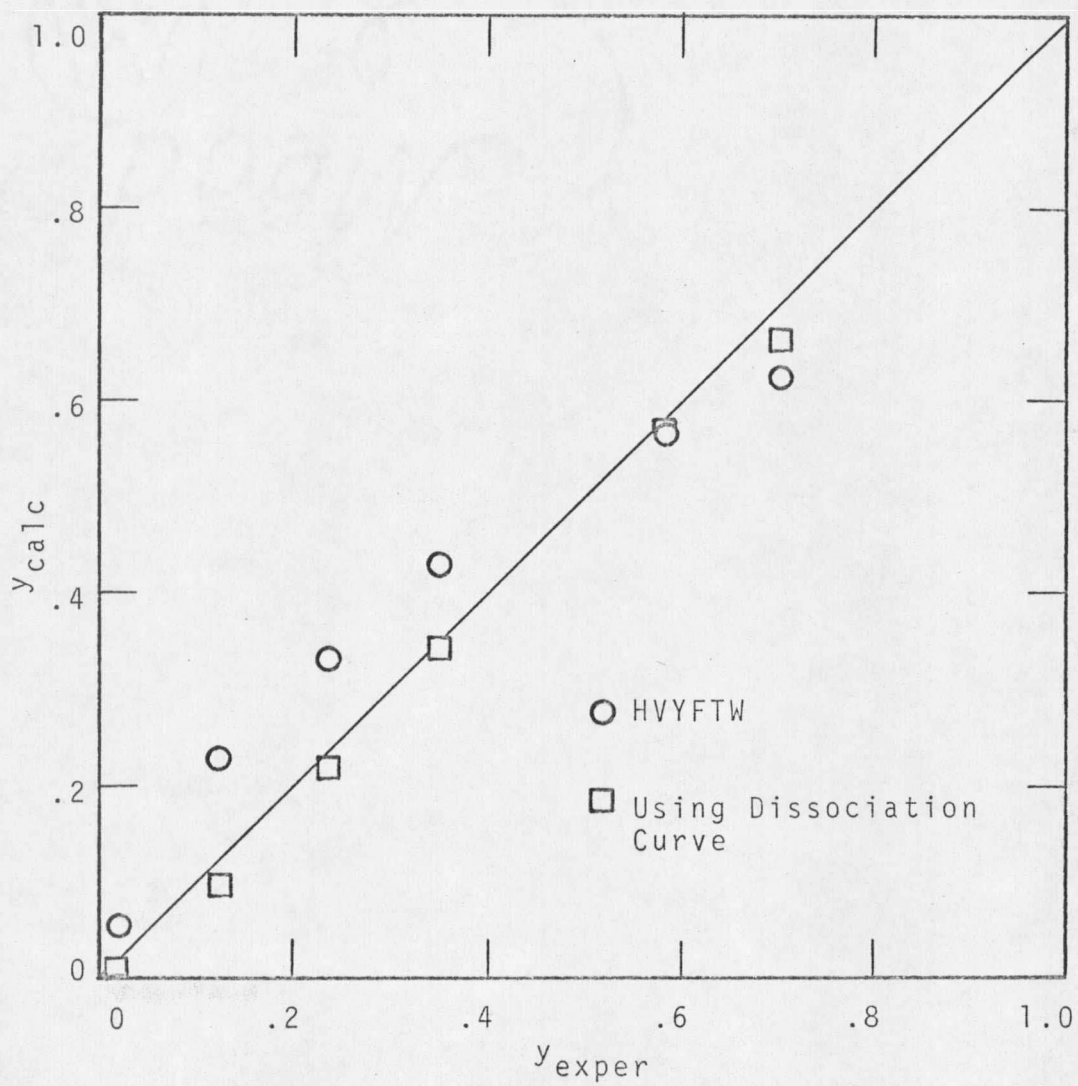


Figure 11. Vapor Compositions for HCl-H₂O at 55.2°C.

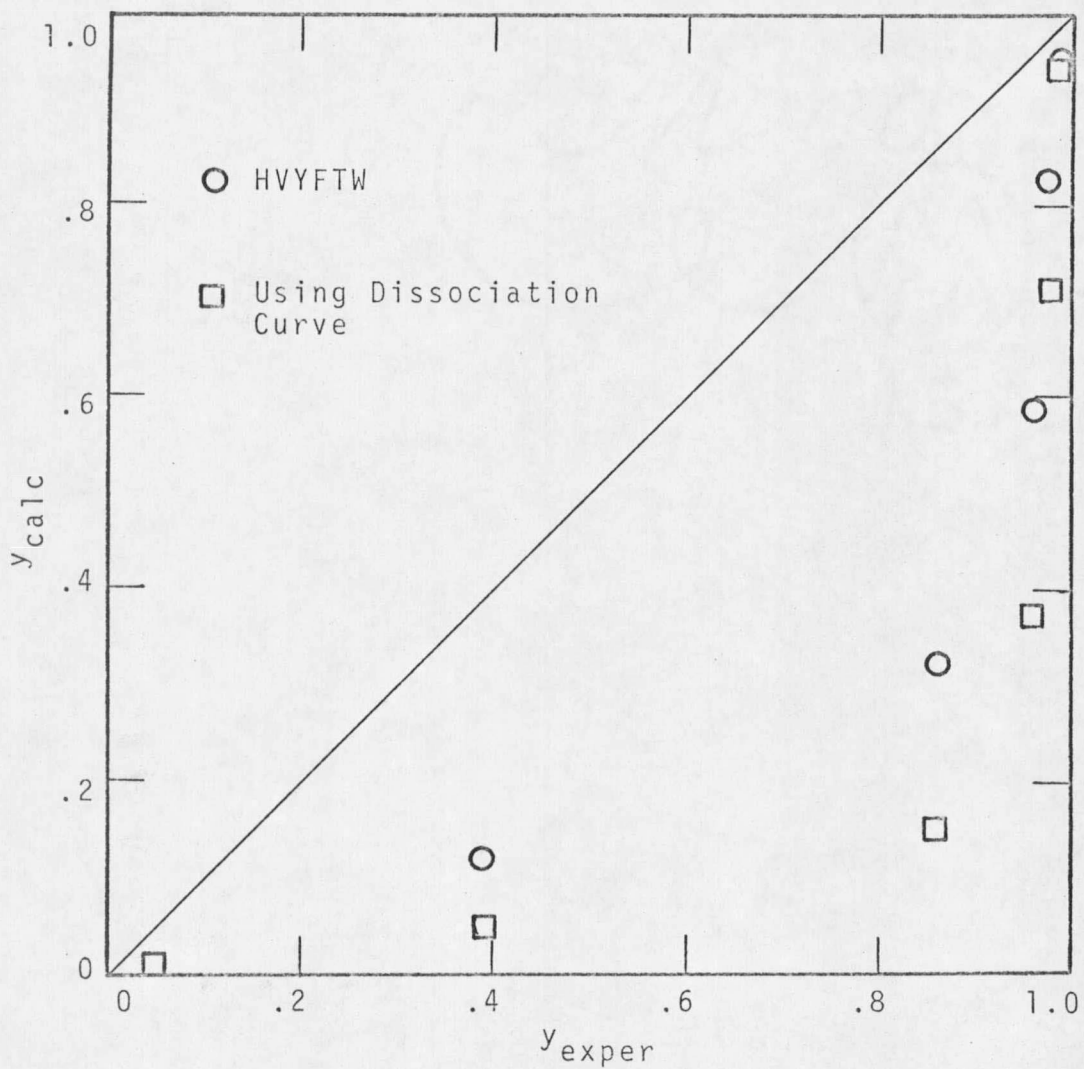


Figure 12. Vapor Compositions for HCl-H₂O at 1.0 atm.

The HCl data was used in the LTFTXW or unsymmetric convention fitting program. The results obtained for this method were poor in all cases as shown in Table I. They were completely inconsistent as the liquid-phase mole fraction, which is calculated and compared to the original, even dropped for some increasing experimental liquid concentrations or it became greater than 1.00. One possible explanation for these poor results is that the data is out of the range of Henry's constant. This could easily be because the HCl data ranges up to a mole fraction of .2. In the example of a supercritical component given by Prausnitz, N_2 in decane, the mole fraction of N_2 in the vapor is nearly 100% for liquid-phase mole fractions of about .04. The HCl vapor phase mole fraction is very low at this liquid concentration. This would indicate that the reference state fugacity for electrolytes should be determined from the pure saturated vapor fugacity.

The solvent-solute interaction parameter, Λ_{21} , was set equal to zero in the unsymmetric convention. This may be a good assumption for nonelectrolytes but not necessarily for electrolytes. The presence of polar molecules and ionic charges may make this assumption invalid.

No dissociation curves were found for the other electrolytes to test this covalent molecule theory as was done for

